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16. ABSTRACT

This report was compiled to provide the Environmental Protection Agency with an assessment of multi-media pollutants from oil shale processing and coal gasification facilities. The report examines oil shale and coal extraction processes in addition to fuel conversion methods. Three oil shale conversion processes are considered: the TOSCO II, Paraho, and Union Oil processes. The Lurgi process is considered for coal gasification. Process descriptions and module definitions are presented for each operation. Potential air emissions, water effluents, and solid wastes are then identified and quantified for each module. Emissions of trace elements and organics are determined qualitatively. An assessment of resources required to support the production facilities is also included. The overall report is presented in two volumes. Volume I summarizes the objectives, the approach, and the results of the study. Volume II gives detailed descriptions of the methodology and the results.

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EMISSIONS FROM SYNTHETIC FUEL PRODUCTION FACILITIES

VOLUME II

September 1977

Prepared for:

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By:

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FOREWORD

The two volumes comprising this document present a study of emissions from synthetic fuel production facilities, performed under EPA Contract No. 68-01-3535. The synthetic fuel production facilities include oil shale and coal extraction, oil shale processing, and coal gasification.

The report presents the best available information. Most of the data for the TOSCO II oil shale process have been previously published and represents widely accepted estimates for the process. Accepted published data for the Union Oil and Paraho oil shale processes are not presently available. The emissions from these processes were estimated in this report based upon similar processes and developer information. Accepted data for the Lurgi coal gasification process have been previously published. As more information on these processes is released, the contents of this report will be updated or subsequent reports will be prepared to present this data.

This work was conducted under the direction of Mr. Terry L. Thoem, Project Officer, Environmental Protection Agency, Region VIII, Denver, Colorado. This study is complemented by another Radian study, "Atmospheric Pollution Potential from Fossil Fuel Resource Extraction, On-Site Processing, and Transportation", EPA-600/2-76-064. The fuel resources considered in that report are coal, oil shale, oil, and gas.

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1.0 INTRODUCTION

In this volume of the report, process descriptions of the synthetic fuels processes are presented along with detailed discussions of the analytical procedures used to define individual modules and to identify their emissions. Descriptions are given for both the resource extraction processes and the synthetic fuel conversion processes. Also included in the report are qualitative discussions of trace element and organic emissions and effluents. In addition, the water systems are analyzed for potential problems in achieving "zero discharge" of water effluents

The information presented in this document is organized into three sections. Oil shale processing is discussed first in Section 2.0. Oil shale extraction modules are presented for surface mining and underground room-and-pillar mining. A module for oil shale sizing is also included. Then oil shale retorting and upgrading modules are discussed. The types of oil shale processes studied are the TOSCO II process, the Paraho process and the Union Oil process.

In Section 3.0 coal gasification processing is discussed. Included are a coal strip mining module and Lurgi coal gasification modules for the production of low-, medium-, and high-Btu gas.

All of the synthetic fuels process facilities are designing for "zero discharge" of water effluents. Section 4.0 examines the proposed water systems for the TOSCO II process and the Lurgi process for potential problems in achieving zero discharge as well as the potential advantages and disadvantages of treatment of water effluents to a quality which may be discharged.

Module Basis

Module sizes for the synthetic fuels processes were selected to represent typical sizes anticipated for a commercial facility. These module sizes also allow the processes to be compared on an energy output basis.

Air emissions, water effluents, energy recovery, and process requirements for water, manpower, and ancillary energy are discussed for each of the modules.

2.0 OIL SHALE PROCESSING

This section of the report presents a description of oil shale surface and room-and-pillar mining along with retorting technologies of the TOSCO II, Paraho, and Union Oil processes. Process modules are defined and emissions from the modules are assessed.

2.1 Oil Shale Extraction

Oil shale deposits in the Colorado River Valley of the Rocky Mountains are considered to be the richest deposits of oil shale in the world. These deposits represent a resource of an estimated two trillion barrels of oil. While development of an oil shale industry in the U.S. has been considered in the past, the discoveries of crude oil in Pennsylvania and later in Texas made oil shale extraction uneconomical (UN-025). Outside the U.S., oil shale has been commercially mined and processed into liquid fuels for many years, usually in areas where domestic supply of crude oil was limited and imports were insufficient.

Oil shale is a marlstone-type inorganic material containing an organic polymer known as kerogen. Kerogen is only slightly soluble in conventional organic solvents. When heated, however, the kerogen decomposes to yield hydrocarbon gases and liquids. These hydrocarbon products can be processed and refined in much the same manner as petroleum. Typical organic and mineral content for oil shale containing 25 gallons of oil per ton of shale is given in Table 2.1-1.

There are two major options considered for oil shale development: 1) mining followed by surface processing of the oil shale and shale oil, and 2) in situ (in place) processing.

Development of either method is expected to proceed in a modular fashion. A full scale commercial size plant is not expected to be in operation prior to the middle or late 1980's.

TABLE 2.1-1. TYPICAL CONSUMPTION OF OIL SHALE SECTIONS AVERAGING 25 GALLONS OF OIL PER TON IN THE MAHOGANY ZONE OF COLORADO AND UTAH

	Weight-percent
Organic Matter:	
Content of raw shale	13.8
Ultimate composition:	
Carbon	80.5
Hydrogen	10.3
Nitrogen	2.4
Sulfur	1.0
Oxygen	5.8
Total	100.0
Mineral Matter:	
Content of raw shale	86.2
Estimated mineral constituents:	
Carbonates; principally dolomite	48
Feldspars	21
Quartz	13
Clays, principally illite	13
Analcite	4
Pyrite	1
Total	100

Source: US-093

Most high quality oil shale lies below a thick layer of overburden containing little or no kerogen. Underground mining techniques will primarily be used to extract these resources. There are some areas, however, where oil shale lies close enough to the surface to permit surface mining.

2.1.1 Oil Shale Surface Mining

Because oil shale zones can be very thick, the typical surface oil shale mine will be an open pit type mine.

Factors affecting the suitability of shale oil surface mining are the amount of overburden that must be removed in order to mine the shale and the availability of a disposal area for the overburden. In comparison with underground mining, surface mining has several economic advantages--surface mining is capable of oil extraction at a lower cost and less manpower is required (HI-083). Also, a greater resource extraction per unit land area is achievable. In addition, surface mining is inherently safer. The main disadvantage is a high land impact since all of the spent shale and solid waste must initially be disposed on the surface. Only after many years may mine back filling commence.

Overburden at potential surface mining sites ranges from 30-250 meters (100-800 feet) in depth, averaging approximately 140 meters (450 feet). Due to the required mine depth, several bench levels must be provided to develop sufficient working forces to meet production rates. An average mine slope of 45° with a working slope of 35° is typical (US-093). Overburden and shale are extracted by drilling and blasting. Blasted raw shale is hauled by trucks to primary crushers in the pit. Shale from the crusher is removed from the mine by conveyor to secondary crushing and screening facilities. The secondary crushing and

and screening facilities may be located at the upgrading plant site. Major processing steps associated with a surface mining operation are shown in Figure 2.1-1.

Emission sources associated with the surface mining facilities include excavation blasting, road dust from transportation of oil shale and overburden, combustion emissions from diesel-powered equipment, primary and secondary crushing operations, and wind blown dust. Primary control for fugitive dust is by water spraying with or without the use of dust suppressants. Particulates generated in the crushing operations may be reduced by wet scrubbers or fabric filters.

Water resulting from mine drainage and shale pile runoff is routed to evaporation-containment ponds. This water may be used for road dust control, shale pile wetting, and particulate control systems. If the mine is close to the upgrading facilities, the mine water may be clarified and used as makeup water for the upgrading facilities. Water initially pumped from the mine should be of good quality; however, the water salinity will probably increase with mine life due to leaching. Another potential demand for mine water is the reclamation operation.

A major environmental problem associated with surface mining is solids disposal. Overburden as well as processed shale must be disposed of on the surface. Initially, overburden and spent shale is hauled off site to some containment area. Overburden may be removed to the containment site by trucks or conveyor. Processed shale may be returned to the containment area by truck, conveyor, or slurry pipeline. Only after mined-out areas of the pit become available can back filling begin. This is expected to be a long time period: up to 30 years. Since solid waste cannot be disposed of underground, the land impact associated with surface mining is higher than with room-and-pillar mining.

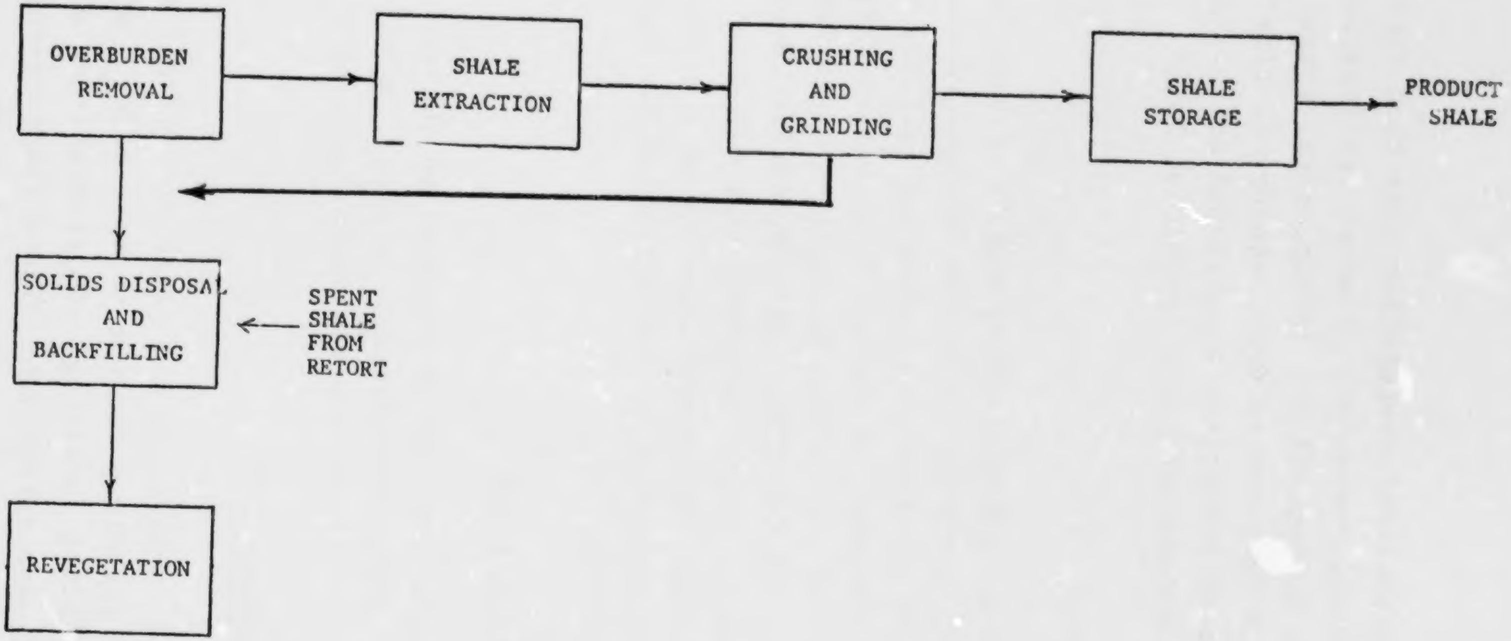


FIGURE 2.1-1 STEPS INVOLVED IN OIL SHALE SURFACE MINING

A land reclamation/revegetation operation should be part of a surface mining operation; however, reclamation procedures are still in conceptual and developmental stages. Reclamation requirements in terms of cost, equipment, time, and water have not yet been accurately established nor has a successful operation been demonstrated on a commercial basis.

2.1.1.1 Module Basis

The oil shale surface mining module is based upon an operation capable of supplying sufficient amounts of run-of-mine oil shale for a shale oil retorting/upgrading facility producing 7950 m^3/day (50,000 bbl/day) of shale oil having an average oil quality of 125 ℓ/MT (30 gal/ton). The mine produces approximately 59,900 MT/day (66,000 TPD). This production equals the demand of the processing plant, assuming that the plant would operate at approximately 90 percent capacity on a yearly basis. Table 2.1-2 contains estimates of the environmental impact of surface oil shale mining.

2.1.1.2 Module Description

This section contains discussions on the processing steps, flow rates, energy requirements, energy recovery ratio, and water requirements of the surface mining operation.

Processing Steps

The steps involved in the extraction of oil shale by the surface mining technique include topsoil removal and storage; overburden drilling, blasting, and removal; and oil shale drilling, blasting, and extraction. These steps resemble those for coal surface mining, however, the pit is much deeper for oil shale surface mining. For this module the average overburden thickness is approximately 137 meters (450 feet). The shale is mined by a quarry-like operation due to the nature of the mine pit area.

TABLE 2.1-2. SUMMARY OF ENVIRONMENTAL IMPACT FROM SURFACE MINING OF OIL SHALE

Basis: 59,900 MT/day of oil shale extracted (66,000 TPD)	
Air emissions (Kg/day)	
Particulates	5,038
SO_2	640
NO_x	8,700
HC	1,000
CO	5,200
Water Effluents	0
Thermal	Neg
Solid Wastes (MT/day)	65,000*
Ancillary Energy (kcal/hr)	1.7×10^8
Energy Recovery Ratio	0.971

*Solid waste is confined to overburden. Spent shale is addressed in oil shale processing.

Flow Rates

The mine facilities extract 59,900 MT/day (66,000 TPD) of raw oil shale. This shale is hauled to the primary crusher located within the pit. For a mine producing this amount of raw oil shale, Hittman reports that approximately 65,000 MT/day (72,000 TPD) of overburden is removed (HI-083).

Energy Requirements

The energy requirements were calculated by scaling up the numbers used in the Hittman report (HI-083) so that they represent the size of this module. The revised numbers are presented in Table 2.1-3.

TABLE 2.1-3. DAILY ENERGY REQUIREMENTS FOR OIL SHALE SURFACE MINING

Operation	Electricity (kWh)	Diesel Fuel* (ℓ)	Total (kcal)
Mining	11.80×10^5	300,615	3.61×10^9
Hauling		65,656	$.57 \times 10^9$
Reclamation		2,810	0.03×10^9
TOTAL =	11.80×10^5	369,081	4.21×10^9

*8630 kcal/liter

Energy Recovery Ratio

The energy recovery ratio for this module was determined by dividing the total heating value of the oil shale extracted (59,900 MT/day or 1.46×10^{11} kcal/day) by the sum of this number and the above module energy requirement (4.21×10^9 kcal). The result gives an energy recovery ratio of 0.971 for oil shale surface mining.

Water Requirements

The water requirements for the surface mining module for dust or particulate control is supplied by water collected in excavated areas. Excess water may be routed to an evaporation pond. The variable climate of the areas underlain by oil shale and lack of conclusive data based on actual revegetation of an appropriate scale of these areas make it difficult to predict the amounts of water needed for reclamation.

2.1.1.3 Module Emissions

The air, water, and solid emissions from oil shale surface mining are presented in this section. These emissions are based upon the module extraction rate of 59,900 MT/day. Primary sources of information for this section of the module include the Environmental Assessment for a Proposed Coal Gasification Project (WY-007) by Wyoming Coal Gas Co. and Rochelle Coal Co. prepared by SERNCO and the Draft Environmental Statement for the El Paso Coal Gasification Project (US-112).

Air Emissions

Major sources of air emissions found within oil shale surface mining include:

- wind erosion
- topsoil removal and storage losses
- drilling overburden and oil shale
- blasting of overburden
- blasting of oil shale
- overburden excavation and loading

- mining roads
- diesel equipment

Table 2.1-4 presents the atmospheric emission estimates for this module. The estimates do not include the effect of control measures beyond basic requirements. The basic requirements assumed include hard surfacing major mine access roads, periodic water spraying of secondary roads as conditions require, and reclaimed mine area contouring to promote vegetation. The effect of these control techniques on the above emis-emissions is highly variable and cannot be estimated.

TABLE 2.1-4. ATMOSPHERIC EMISSIONS FROM OIL SHALE SURFACE MINING
Basis: 59,900 MT/day (66,000 TPD) oil shale mined

Operation	Emissions (kg/day) Part	SO_2	NO_x	HC	CO
Wind erosion	45				
Topsoil removal and storage losses	6				
Drilling	102				
Blasting of overburden	757				
Blasting of oil shale	93				
Overburden excavation	2445				
Mining roads	1300				
Diesel equipment	290	640	8700	1000	5200
TOTAL =	5038	640	8700	1000	5200

Wind erosion results in the discharge of particulates from the exposed mine areas. Using a wind erosion equation developed by PEDCo-Environmental, an emission factor of 0.60 MT/acre-yr is calculated. Assuming 28 acres per year are disturbed, approximately 45 kg/day (100 lb/day) of particulates are emitted (CO-352, US-093).

Topsoil removal and its storage is the first operation in overburden excavation. SERNCO estimated that topsoil removal discharges roughly 76 kg/acre-yr of topsoil disturbed. This amounts to around 6 kg/day (13 lb/day) of dust emitted to the air from this operation, assuming 28 acres per year are disturbed due to mine development (US-093).

Blast hole preparation by drilling releases noticeable amounts of particulates during overburden removal. Adjusting the number given by SERNCO for overburden drilling emissions to an estimate which reflects the materials removal rate in this module, it is estimated that 102 kg/day (227 lb/day) of particulates are emitted.

The blasting of the overburden discharges significant quantities of dirt and dust into the air, however, this operation occurs only periodically. Adjusting the estimates by SERNCO for overburden blasting, roughly 757 kg/day (1677 lb/day) of particulates less than 10μ in diameter are discharged to the atmosphere. This number is based on the assumption that the large diameter particles settle out in the immediate vicinity of the mine.

Following blasting, the overburden is loaded for removal from the pit area. This phase of mining is the largest single source of particulates in the extraction operation. SERNCO estimated that approximately 0.035 kg of dust is emitted per metric ton of overburden removed. Assuming a daily removal rate of 64,450 MT/day, the resulting emissions will be about 2260 kg/day (4980 lb/day).

The fragmenting of the oil shale by blasting periodically releases some dust to the air. Assuming the same amount of dust is emitted for the blasting of the oil shale as for coal (0.0016 kg/MT of material mined), then 93 kg/day (206 lb/day) of dust are emitted (WY-007).

The diesel-powered vehicles operating in the pit emit significant quantities of pollutants. The equipment consumes approximately 82,000 liters/day (21,600 gal/day) of diesel fuel (adjusted value obtained from Hittman Report) (HI-083). The emissions were determined by applying EPA emission factors for heavy duty diesel engines (EN-071).

Hauling the extracted shale and overburden on mine roads results in the dispersion of dust from both payloads and road surfaces. Adjusting emission estimates reported by SERNCO for coal mine road dust gives a total particulate discharge rate of roughly 1300 kg/day (2900 lb/day) for the hauling of the oil shale and overburden.

Water Emissions

All mine water is collected and used for dust or particulate control with any excess being routed to an evaporation pond. Therefore, no liquid effluent streams are anticipated. Since no water is discharged, no thermal impact is expected.

In later years, water accumulation from spent shale backfilling and supplemental irrigation from reclamation activities could infiltrate through faults and cracks into underground aquifers. The exact impact of the infiltrating water on an aquifer would depend upon local geological conditions.

Solid Wastes

For a surface mine producing 59,900 MT/day of raw shale, approximately 64,450 MT/day (70,900 TPD) of overburden must be disposed (HI-083). This quantity represents the solid waste generated by this module.

2.1.2 Underground Room-and-Pillar Oil Shale Mining

Most actual experience in oil shale mining involves underground mining. The Bureau of Mines has demonstrated the feasibility of room-and-pillar mining for oil shale at its facility near Rifle, Colorado.

Entry to a room-and-pillar mine may be by horizontal adit or by shaft. Early work was done on adit entry because this is the less expensive method. It will be necessary to use shaft entry on most of the high-quality shale reserves. Entries to a production zone, though larger than those found in coal mines, have been dug using conventional drilling, blasting, and loading equipment and techniques. In a commercial-scale mine, moles and other advanced cutting machines might be used. All portions of the mining cycle of drilling, charging, blasting, wetting of rock piles, loading, hauling, scaling, and roof bolting will be going on concurrently in various areas of the mine except that blasting will occur during shift changes. At no time will personnel be allowed in the immediate area of the blasting.

The room-and-pillar mine offers an efficient proven method for mining hard materials deep underground. The rooms and pillars will be on the order of 18 meters (60 feet) square with about 18 meters (60 feet) spacing and the floor-to-ceiling clearance will be about 18 to 24 meters (60 to 80 feet). The mining can be done in two levels. First, the upper 9 meters (30 feet) or so are removed; then deeper cuts are made in selected areas. When the mine is in full operation, extraction proceeds on both levels at the same time.

Rotary drills prepare holes for blast charges which fragment a part of the oil shale zone. Water and wetting agents can be applied at the drill for dust control. Detonation of explosives produces quantities of carbon monoxide, nitrogen oxides, and dust. Some of the dust will be carried away by ventilation air. After fragmentation, the shale is loaded onto a large truck or conveyor by a front-end loader and moved to a crushing facility. Water will be added to the broken rock prior to and during loading and conveying to minimize dust. This wetting operation is one of the major consumers of water in the mining operation. Water application will be minimized to reduce runoff from the pile of broken rock.

Roof support must be provided for the rooms excavated. The system most frequently used involves drilling holes in the roof and inserting bolts equipped with either expansion heads or other fastening systems. Roof bolts generate compressive stresses to strengthen the roof, and they permit excavating larger rooms than would otherwise be possible.

The mine ventilation system will draw air into the mine from the mine entry and distribute it to the work areas. The mine ventilation requirements are 3 m^3/min (100 cfm) of air per diesel horsepower.

Water resulting from surface mine drainage and shale pile runoff is also routed to evaporation/containment ponds. Potential uses for this water have been discussed in the oil shale surface mining section (2.1.1).

Although the extracted material is almost entirely oil shale, the oil content of the oil shale may vary considerably. A mining zone contains layers of varying quality. Generally, a zone consists of a thick sequence of layers with an average yield of 30+ gallons of oil per ton of shale. Large layers of lower yield oil shale are treated as overburden, but ordinarily no attempt is made to separate material within a zone into high- and low-quality shale.

Leaving pillars in place to support the roof significantly decreases the portion of the oil shale that can be mined. About 60 percent of the oil shale in place is recovered in room-and-pillar mines.

A major problem associated with oil shale extraction involves solids waste handling and ultimate disposal of the spent shale. Shale increases in size by about 12 vol. % during processing (US-093). Processed shale may be back-filled in an underground mine, substantially reducing the impact of the surface disposal problem. During the first three years of production, all processed shale would be disposed on the surface. After this time period sufficient underground space would be available for partial disposal (US-093). This is a major environmental advantage of underground over surface mining. The exact amount of back-fill depends on the type of spent shale, degree of compaction, moisture content, and mine volume used. Currently, only one oil shale mining plan calls for mine back-filling.

Spent shale may be returned to the mine by trucks, conveyors, or a slurry pipeline. If slurried, the slurry water has to be collected in the mine and returned to the surface. If a portion of the spent shale cannot be accommodated underground or if none of it is back-filled, it must be contained on the surface. Land must be available for disposal of both the overburden from the mine opening and the spent shale.

Surface disposal of solid waste may be achieved by containment (box canyons) and/or isolation (mesas), followed by reclamation. Land reclamation and revegetation is a necessity for reducing the land impact of the shale oil industry. Procedures required to properly restore and revegetate the land have not been adequately demonstrated. Total cost, time, and water requirements have not been accurately established.

2.1.2.1 Module Basis

The oil shale underground room-and-pillar mining module is based upon an operation capable of supplying sufficient quantities of raw oil shale to support a shale oil retorting/upgrading facility producing 7950 m^3/day (50,000 bbl/day) of shale oil. The mine produces approximately 59,900 MT/day (66,000 TPD) of oil shale having an average oil quality of 125 ℓ/MT (30 gal/ton). This production equals the demand of the processing plant, assuming that the plant would operate at approximately 90 percent capacity on a yearly basis. Table 2.1-5 presents a summary of the environmental impact of the oil shale underground mining model.

2.1.2.2 Module Description

This section contains discussions concerning the processing steps, flow rates, energy requirements, energy recovery ratio, and water requirements of the underground mining operation.

TABLE 2.1-5. SUMMARY OF ENVIRONMENTAL IMPACT FROM ROOM-AND-PILLAR MINING OF OIL SHALE

Basis: 59,900 MT/day of oil shale extracted (66,000 TPD)	
Air (kg/day)	
Particulates	665
NO_x	2945
HC	590
CO	5180
SO_2	Neg
Water Effluents	0
Thermal (kcal/hr)	Neg
Solid Wastes	Neg
Water Requirements (ℓ/min)	1430
Ancillary Energy (kcal/hr)	9.2×10^6
Energy Recovery Ratio	0.998

Processing Steps

The mining will proceed by the conventional mining cycle of drilling, charging, blasting, wetting of rock piles, loading, hauling, scaling, and roof bolting. All phases of the cycle will be taking place concurrently in various areas of the mine, except that blasting will occur during shift changes when personnel will not be in the immediate area.

Flow Rates

The mine extracts an average of 59,900 MT/day (66,000 TPD) of raw oil shale. This shale is hauled by truck to the primary crusher located on the mine floor.

Energy Requirements

The energy requirements were calculated by scaling up the numbers used in the Hittman report (HI-083) so that they represent the size of this module. The revised numbers are presented in Table 2.1-6.

TABLE 2.1-6. DAILY ENERGY REQUIREMENTS FOR OIL SHALE UNDERGROUND MINING

Operation	Energy Required (kcal)
Mining	91.9×10^6
Hauling	$\underline{129.2 \times 10^6}$
Total	221.1×10^6

Energy Recovery Ratio

The energy recovery ratio for this module was determined by dividing the total heating value of the oil shale extracted (59,900 MT/day or 1.46×10^{11} kcal/day) by the sum of this number and the above module energy requirement (2.211×10^8 kcal/day). The result gives an energy recovery ratio of 0.998 for the underground extraction of oil shale.

Water Requirements

The water requirements for this module consist only of the water required for dust control. It will be used for wetting down blasted shale, mine roads, and drilling dust suppression. The Draft Environmental Impact Statement by the

Colony Development Operation estimates that 1430 liters per minute (380 gpm) of water are needed for this control (US-291).

2.1.2.3 Module Emissions

This section reviews the air, water, and solids emissions expected from the underground mining of oil shale. These emissions are based upon the module extraction rate of 59,900 MT/day (66,000 TPD) of raw shale. The primary source of information for this section was the Draft EIS by the Colony Development Operation in Colorado (US-291).

Air Emissions

There are two sources of atmospheric pollutants from the underground mining of oil shale. The first source is the diesel exhaust fumes generated by mobile mine equipment. Catalytic scrubbers mounted on the equipment remove essentially 100% of the SO_2 emitted. The other source is the various mining activities which discharge fugitive dust to the mine air. Approximately 10 to 15 kg/hr (22-33 lb/hr) enters the mine atmosphere from drilling, hauling, and loading and is drawn into the ventilation system. For three 1-hour periods each day, during blasting, an estimated 100 to 150 kg/hr (220-330 lb/hr) of particulates will enter the mine atmosphere. Reported particulate emission rates are based on an average rate of 28 kg/hr. No particulate control devices are placed on the mine vent. Total emission rates from the mine ventilation system are listed in Table 2.1-7.

Water Emissions

All mine water is collected and used for dust control with any excess being routed to an evaporation pond. For this reason, no water thermal discharges are shown for this module.

TABLE 2.1-7. ATMOSPHERIC EMISSIONS FROM UNDERGROUND OIL SHALE MINING

Basis: 59,900 MT/day (66,000 TPD) Oil Shale Mined

Pollutant	Emission Rate (kg/day)
Particulates	665
Hydrocarbons	590
NO_x	2945
CO	5180
SO_2	Neg

Source: US-291

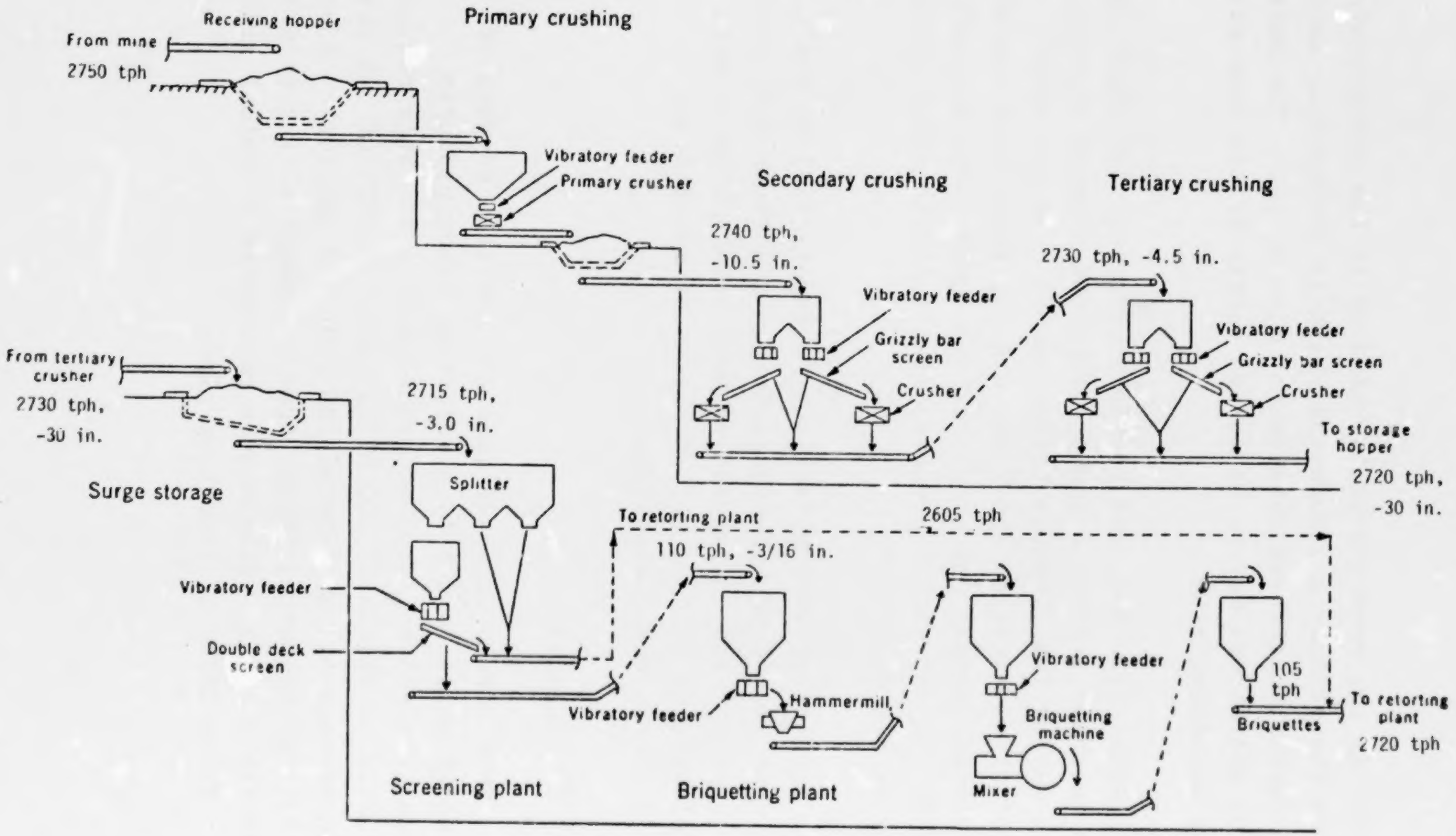
Solid Wastes

Negligible solid wastes are created as a direct result of mine operation since no overburden is removed. The spent shale which is disposed of in the mine is assumed to be a solid waste emission from the retorting plant and not the mine.

2.1.3 Oil Shale Sizing Operations

Much of the mined oil shale will require crushing and sizing prior to retorting. Sizing operations performed on oil shale may include primary, secondary, and tertiary crushing; screening; and briquetting. The required size of the crushed oil shale depends on the specific retorting process being used. The TOSCO II retort requires that the shale be ground to less than 1.2 cm while the Union and Paraho retorts can accomodate ore up to 8.5 cm. Typical operations in a shale sizing facility are shown in Figure 2.1-2.

In order to minimize costs of transporting the raw shale, the crushers are located close to the blasting operation,



Source: US-093

FIGURE 2.1-2 SHALE SIZING OPERATIONS

usually within the room-and-pillar mine or in the surface mining pit. From the primary crushers the shale is conveyed to secondary and tertiary crushers outside the mine or pit. The remaining sizing operations may be performed either at the mine site or at the retorting site.

After secondary and tertiary crushing, the shale is conveyed to shale storage hoppers. From the storage hoppers, the shale may be fed directly to the retort. If the retort cannot accept fine particles the fines are separated from the shale by a screening process and compacted and formed into briquettes suitable for routing to the retort along with the other shale feedstock or are discarded.

The entire sizing facility is a potential source of fugitive dust emissions. Particulate control techniques such as water spraying and shale wetting must be utilized as well as control systems such as wet scrubbers or bag filters in order to minimize dust emissions.

2.1.3.1 Module Basis

This module is based upon an operation capable of sizing enough shale to supply a retorting plant producing 7950 m^3/day (50,000 bbl/day) of crude shale oil. This requires the operation to handle 59,900 MT/day (66,000 TPD) of oil shale having an average oil quality of 125 ℓ/MT (30 gal/ton). A summary of the environmental impact from oil shale sizing is presented in Table 2.1-8. This module represents a typical sizing operation for a TOSCO II retorting plant.

2.1.3.2 Module Description

This section contains discussions concerning the processing steps, flowrates, energy requirements, energy recovery ratio, and water requirements of the sizing operation.

TABLE 2.1-8. SUMMARY OF ENVIRONMENTAL IMPACT FROM OIL SHALE SIZING

Basis: 59,900 MT/day of oil shale sized

Air Emissions	kg/day
Particulates	731
Water Effluents	0
Thermal (kcal/hr)	Neg.
Solid Waste	Neg.*
Water Requirements	Neg.
Ancillary Energy (kcal/hr)	16.0×10^6
Energy Recovery Ratio	0.997

*Solid wastes will be negligible for the TOSCO II process, but for Paraho and Union processes, the fines will have to be disposed or consumed by briquetting or by using a combination of retorts, such as TOSCO II, that can consume the fines. If the fines are disposed, they will be produced at a rate of 3000 MT/day (MC-238).

Processing Steps

The steps involved in the sizing of the mined oil shale are primary, secondary, and tertiary crushing and screening. The primary crushing will be done at the mine. Final crushing will be performed near the retorting and upgrading facility.

The crushing operation is designed to maintain a continuous feed to the retort. This objective will be accomplished in part by maintaining a storage pile of coarse ore and a storage bin of fine ore. No storage facility for run-of-mine ore will be needed. The mine haulage operation is entirely dependent on the operation of the primary crusher. Should a breakdown occur in the primary crusher or the conveyor to the coarse ore storage, haulage from the mine will be interrupted. To avoid shutdown of the retorting and upgrading facilities, sufficient storage of coarse ore will be maintained to allow uninterrupted operation of the downstream processing facilities for about one month. If the final crusher breaks down, the amount of stored fine ore will be enough to operate the retort for approximately 5 hours.

Flow Rates

The capacity of the primary crusher and the conveyor to the coarse ore stockpile will be 4285 MT/hr (4750 tons/hr). Because of the periodic nature of the mining and primary crushing operations, the coarse ore storage will provide surge capability to maintain a uniform feed rate to the final crusher in addition to providing an emergency supply in case of interruption in the supply of coarse ore from the mine and primary crusher. Normally, the coarse ore from the primary crusher will be fed directly to the final crusher at a rate of 2685-2885 MT/hr (2950-3250 tons per hour). During periods when the coarse ore production exceeds the feed requirements of the final crusher, the excess will be diverted to coarse ore storage. A coarse ore reclaim system will be provided to maintain a uniform feed rate to the final crusher. Ten crushers in the final crushing facility will produce minus 1.27 cm (0.5 in) shale on a continuous basis at a rate of 2685-2885 MT/hr for feeding to the retort.

Energy Requirements

All crushing and conveying equipment will be driven electrically and consume about 445,000 kWh daily (382.4×10^6 kcal/day) (US-291).

Energy Recovery Ratio

The energy recovery ratio for this module was determined by dividing the total heating value of the oil shale sized (59,900 MT/day or 1.46×10^{11} kcal/day) by the sum of this number and the above module energy requirements (382.4×10^{6} kcal/day). The result gives an energy recovery ratio of 0.997 for the sizing of oil shale.

Water Requirements

The water requirements for this module will be negligible if primary dust control is accomplished by the use of bag filters. If wet scrubbers or dust suppression sprays are used the requirement will increase slightly.

2.1.3.3 Module Emissions

This section reviews the emissions and effluents expected from an oil shale sizing operation. The major impact will be to the air quality, while little or no water or solid impact is anticipated. The primary source of information for this section was the Draft EIS by the Colony Development Operation in Colorado (US-291).

Air Emissions

The major sources of atmospheric emissions from oil shale sizing operations include the crushing and screening facilities, belt conveyor transfer points, and the fine ore storage silo. Table 2.1-9 summarizes the emissions from these areas.

TABLE 2.1-9. ATMOSPHERIC EMISSIONS FROM OIL SHALE SIZING

Source	Particulate Emission Rate (kg/day)
Primary Ore Crusher	93
Portal Transfer Point	12
Feed Bin Transfer Point	70
Reclaim Transfer Point	70
Fine Ore Crusher	431
Fine Ore Storage	55

All crushing and screening facilities will be controlled by the use of fabric filters, with an assumed collection efficiency of 99 percent. The stack emissions from the filter vents used on the primary crusher and screener will be discharged at the rate of 3.62 kg/hr of particulates according to the Colony Development's EIS (US-291). The fine ore crushing facility will also be controlled by the use of fabric filters. The reported particulate emissions from the fine ore crusher will be 16.6 kg/hr according to Colony.

Coarse ore from the primary crusher located in the mine is discharged to an inclined conveyor system for transport to the coarse ore storage site or the final crushing plant, where secondary and tertiary crushing occurs. Emissions from the three transfer points along the enclosed conveyor are 5.9 kg/hr of particulates, as seen in Table 2.1-9.

Prior to being fed to the retorts, the sized shale is stored in one of three large storage silos which serve as surge capacity. Particulate emissions from the storage silos are controlled with fabric filters. Particulates are emitted at the rate of 2.1 kg/hr from the filter stacks according to Colony.

Water Emissions

There are no process water requirements or water effluents from oil shale sizing operations. Thermal discharges are therefore non-existent. Dust suppresion sprays may be used, as an alternative, at transfer points.

Solid Wastes

Minimal solid wastes are generated from oil shale sizing operations for the TOSCO process, but for Union and Paraho processes the fines will have to be disposed or consumed by briquetting or using a combination of retorts, such as TOSCO, that can consume the fines. If the fines are disposed, they will be produced at a rate of 3000 MT/day (3300 TPD) (MC-238).

2.2 Shale Oil Processing

There are two stages involved in the processing of oil shale. First, the oil shale is heated to form hydrocarbon gases and liquids by pyrolysis or retorting. The shale oil is produced by simply providing thermal energy to cleave enough bonds in the kerogen matrix to allow the cracked products to be volatilized and later condensed as oil. In the second stage, the shale oil is upgraded for transportation and for subsequent use in refineries or by consumers.

This report concentrates on three processes, the TOSCO II process, the Paraho (indirect mode) process, and the Union Oil Retort B process. These three processes represent different approaches to oil shale processing and have been tested to varying degrees in demonstration facilities. This report does not intend to imply that these or any other oil shale processes are more or less technologically or environmentally feasible.

As yet, no commercial-sized facilities have been constructed. Colony Development Operation has prepared an environmental impact analysis (CO-175) for a 7950 m^3/day (50,000 bbl/day) shale oil production facility using the TOSCO II oil shale retort. A more recent environmental impact statement for the proposed oil shale facility by Colony has been published by the Department of Interior (US-291). Since no detailed emission information such as an EIS has been prepared for the Paraho or Union Oil processes, the process representatives were contacted to obtain emission rates. Gaps in emission data occur since the processes are still in early stages of development. Available information is mainly concerned with EPA criteria pollutants, SO_x, NO_x, CO, particulates and total hydrocarbons. Little information is available concerning emission rates of specific trace elements and organics; however, studies are currently underway or are in the planning stages. Due to the lack of information, this report presents qualitative rather than quantitative discussions of trace elements and organics.

A general discussion of oil shale processing, given below, is followed by detailed descriptions of three individual processes and their modules.

Retorting (Pyrolysis) Techniques

Shale oil retorting may be grouped into two broad categories:

- those which mine and then retort the shale above ground (ex situ), and
- those which retort the shale in place underground (in situ).

This report discusses only ex situ processes. Ex situ processes make use of more familiar technology and consequently are more advanced. The intriguing advantage of in situ processing is that the massive solids handling and disposal problems associated with ex situ processes may be avoided.

Ex situ processes require a retort, solids handling facilities, and shale oil upgrading facilities. Of these processes, only the retorting represents new technology that must be developed. The shale oil upgrading can be accomplished using conventional petroleum refining techniques, although research is being conducted in several areas of the upgrading facilities specifically related to shale oil processing requirements.

Current ex situ processes incorporate either solid-solid or solid-gas heat transfer. The TOSCO II process utilizes solid-solid heat transfer in the form of hot ceramic balls to supply heat to the oil shale. The ceramic balls are heated internally and then mixed with the raw shale in the retort. After retorting, the ceramic balls must be separated for recycle from the spent shale. Other processes use sand or spent shale particles. Ex situ processes which involve gas-solid transfer either use internal gas combustion or external heat generation. The Paraho (direct mode) and Union Retort A processes use internal gas combustion by injecting air directly into the retort. The heat liberated by the combustion of fuel gas and carbon residue provides the required retorting temperatures. The Paraho (indirect mode) and Union Retort B processes use external heat generation from external heaters to provide a high temperature recycle gas which is routed to the retort. The recycle gas raises the shale to the retorting temperature of approximately 480°C (900°F). Combustion does not occur in the retort as it does with internal gas combustion processes.

Upgrading Techniques

Many common features exist in the various shale oil processes. These common features result from the fact that certain basic processing steps must be performed to obtain a marketable hydrocarbon product from oil shale. These steps include retorting, oil recovery and fractionation, gas recovery and treating, sulfur recovery, cracking heavy fractions, hydrotreating hydrocarbon fractions, ammonia separation, and water treating. Different shale oil processes use the same established technology for all operations except the retorting step. Although the effluent stream from retort types differ, the same upgrading processes can be used.

A typical shale oil upgrading sequence is as follows:

1) Effluent from the retort is cooled, allowing separation of light gases overhead and removal of water by use of knockout drums. The crude shale oil is routed to a fractionator for product separation. A typical fractionator separates the feed stream into gas, sour water, naphthas or light oil, and a heavy bottoms oil. A series of parallel operations follows the fractionation as product streams are upgraded and by-products recovered.

2) All gas streams produced in oil shale refining are routed to a gas recovery and treating unit. In this unit, heavy hydrocarbons (C_5^+) are recovered and returned to the light oil stream

from the fractionator for processing. The gas is treated in an amine or other similar unit for removal of hydrogen sulfide and carbon dioxide. The clean gas may then be routed to boilers for power generation or to a methane/steam reformer for hydrogen generation. The acid gas is stripped from the amine and routed to a sulfur recovery unit.

3) The sulfur recovery unit normally consists of a Claus plant working in conjunction with a tail gas treating unit. This unit should be capable of 99% sulfur recovery (HI-083). If the hydrogen sulfide concentration in the Claus feed is maintained at 40 vol. % or higher, a three-stage Claus plant should recover approximately 95% of the equivalent sulfur in the charge. The gas stream containing approximately 5% of the original sulfur is routed to a tail gas treating unit. Performances of tail gas treating units vary; however, approximately 95% of the remaining sulfur should be removed. Some tail gas units reduce sulfur to the level of 250 ppm SO_2 in the effluent gas stream.

4) Light distillate from the fractionator requires hydrotreating to remove impurities and to improve pour point and viscosity. Since hydrogen is required, a hydrogen generation unit is normally located on site. Hydrogen may be produced from plant fuel gas and steam in a conventional steam reforming process. Hydrotreated oil is routed to product tankage. Sour gas from the hydrotreater is routed to the gas recovery facilities.

5) Fractionator bottoms are routed to a delayed coker for recovery of additional oil by thermal cracking. Oil from the delayed coker is routed to a gas oil hydrotreater. Gas produced from the thermal cracking is routed to the gas recovery facilities. A large percentate of the charge to the delayed coker is produced as coke. This coke may be either marketed as a by-product or used for process heat.

6) An ammonia separation unit is used to remove the ammonia from the hydrotreater wash water. The water is first stripped of any light hydrocarbons which are routed to the gas treating facilities. The ammonia is then removed by an ammonia stripper and compressed to form lqiuid ammonia.

7) Water treating facilities are necessary to all shale oil processing units. Careful water management and coordinated water-treating facilities are required to reduce makeup water requirements and to prevent water pollution. Maximum reuse is anticipated if a goal of zero wastewater discharge is to be obtained. Water-treating facilities include mechanical draft cooling towers, strippers to remove NH_3 and H_2S, API separators, biological treating facilities, and containment/evaporation ponds.

Characteristics of Plant Streams

The retort is the heart of the shale oil process. Most of the differences that exist between processes are a result of the retorting procedure. Specific retort requirements dictate how fine the ore must be crushed. The TOSCO retort requires ore ground to less than 1 cm (0.5 in.) while the Union and Paraho retorts can receive ore up to 9 cm (3.5 in.) in diameter. Operating conditions of the different retorts vary. This affects the product streams. A comparison of the effluent oil from three retorts is shown in Table 2.2-1.

TABLE 2.2-1. CHARACTERISTICS OF CRUDE SHALE OILS

	Retorting Process		
	Internal Combustion	Indirectly Heated	
	Union Retort A	TOSCO[1]	Paraho (indirect mode)
Gravity, °API	20.7	28.0	21.7
Sulfur, wt. %	0.77	0.80	-
Nitrogen, wt. %	2.01	1.70	-
Pour Point, °F	90	75	65
Viscosity, SUS	223 @ 100°F	120 @ 100°F	68 @ 130°F

[1] Unpublished information submitted by Colony Development Operation indicates TOSCO crude shale oil may have gravity as low as 21° API and sulfur content of 0.75 wt. %.

Source: US-093

Gases produced in shale oil processes vary significantly, depending on the type of retort. Gases from internal combustion retorts such as Paraho (direct mode) and Union Retort A are diluted with combustion products and the inert components of air. As a result, the gas has a low heating value, 900 kcal/Nm^3 (100 Btu/scf). and would be uneconomical to transport a significant distance. Gas from retorts which use indirect heating, such as TOSCO II, Paraho (indirect mode) and Union Retort B, is composed only of undiluted products from the kerogen and has a substantially higher heating value, 8000 kcal/Nm^3 (900 Btu/scf).

The sulfur generated in the retorting step is also dependent upon the type of retorting process used. Retorts using indirect heating, such as TOSCO II, liberate sulfur as H_2S. H_2S is then treated by a gas recovery and treating unit and sent to a sulfur recovery plant where it is recovered as sulfur. Internal combustion retorts also liberate H_2S. A large portion of the uncondensable gases is returned to the retort as combustion gas where H_2S is ignited to form SO_2. However, since shale rock is mainly dolomite limestone, much of the SO_2 is absorbed by the rock and removed with the spent shale. A comparison of gases from internal combustion and indirect heat retorts is shown in Table 2.2-2.

Physical properties and quality of the spent shale also change with the retort. The amount of carbonaceous material remaining on the shale is inversely proportional to the retort temperature. The shale from a low-temperature TOSCO retort contains 5-6% carbonaceous material while the shale from higher temperature retorts have very little residual carbon remaining. Retorts operating at intermediate temperatures, such as the Paraho (indirect mode) retort, and Union Retort B, usually produce shales containing about 3% carbonaceous material.

Regardless of the retort types, all processes can use cracking and hydrotreating processes to upgrade the retort oil to distillate fuel quality. Properties of an upgraded shale oil are shown in Table 2.2-3.

TABLE 2.2-2. CHARACTERISTICS AND YIELDS OF UNTREATED RETORT GASES

	Type of Retorting Process			
	Internal Combustion		Indirectly Heated	
Composition, vol. %	[2]	[2]	As Produced	After Desulfurization
Nitrogen[1]	60.1	62.1	--	--
Carbon Monoxide	4.7	2.3	4.0	4.2
Carbon Dioxide	29.7	24.5	23.6	24.8
Hydrogen Sulfide	0.1	0.1	4.7	(0.02)
Hydrogen	2.2	5.7	24.8	26.0
Hydrocarbons	3.2	5.3	42.9	45.0
Gross Heating Value, Btu/scf	83	100	775	815
Molecular Weight	32	30	25	24.7
Yield, scf/bbl oil	20,560	10,900	923	880

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[1] Includes oxygen of less than 1.0 volume percent.

[2] First analysis reflects relatively high-temperature retorting in comparison with second, promoting higher yield of carbon oxides from shale carbonate and relatively high yield of total gas.

Oil from the retort.

Source: US-093

TABLE 2.2-3. CHARACTERISTICS OF UPGRADED SHALE OILS

Gravity °API	46.2
Sulfur wt. %	0.005
Nitrogen wt. %	0.035
Pour Point °F	<50.
Viscosity, SUS at 100°F	40.

Source: RA-R-215

2.2.1 TOSCO Process

The TOSCO II process features a rotary-type retort which employs ceramic balls to supply the retorting heat by solid-solid heat transfer. A simple flow diagram of the TOSCO retorting step is shown in Figure 2.2-1. Crushed raw shale feed of minus 0.5 inches in size is fed from a surge hopper to a raw shale preheater. The incoming shale is preheated in a fluidized bed to approximately 260°C(500°F) by combining with incoming hot flue gas from the ceramic ball heater. The preheater effluent is routed to a separator in which the shale is settled from the flue gas. Following shale separation, the cooler flue gas, which has been incinerated within the preheat system to reduce trace hydrocarbons, is passed through a high-energy venturi to remove shale dust before being vented to the atmosphere at a temperature of 50-55°C (125-130°F).

Preheated raw shale from the cyclone separators is routed to the rotary drum retort. High-alumina content ceramic balls of one-half inch diameter are combined with the raw shale in the retort. The balls have been heated to approximately 650°C (1200°F) in a furnace fired by product fuel gas. Retort temperature is maintained at 480°C (900°F) with about two tons of

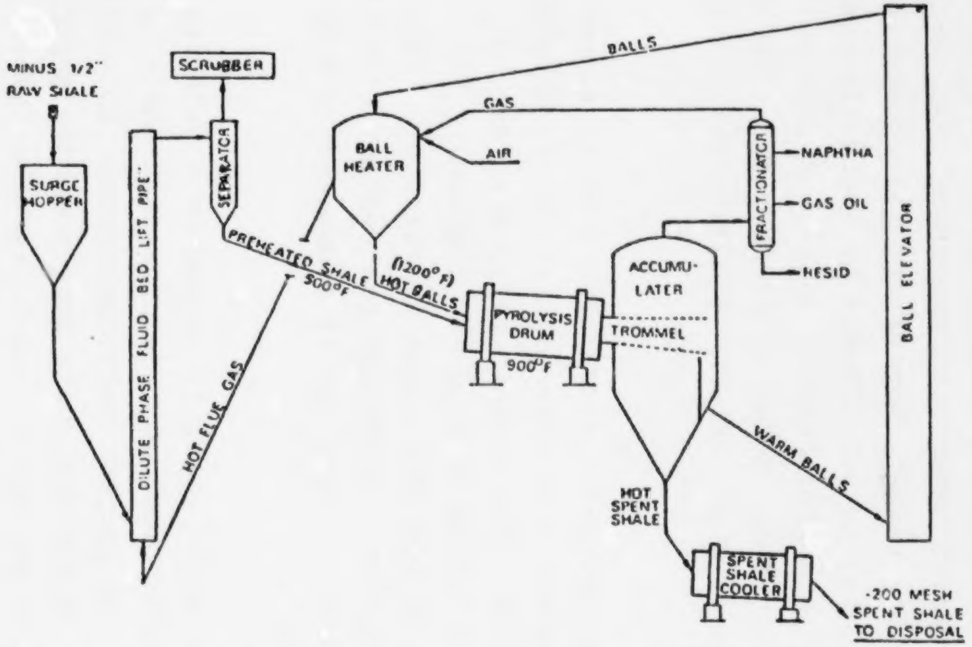

FIGURE 2.2-1 TOSCO II RETORTING PROCEDURE

ceramic balls required to heat one ton of shale. An internal pressure of .35 kg/cm^3 (5 psig) is maintained to prevent the entrance of air. The rotating retort is essentially a ball mill: As the kerogen decomposes, the shale oil loses strength and is pulverized by the ceramic balls. Approximately 5-6% carbonaceous material remains on the shale. An advantage of using indirect heating rather than direct gas combustion is that the fuel gas produced is not diluted by combustion products and consequently has a higher heating value. Approximately 150 Nm^3 of flue gas per cubic meter of product oil (900 scf/bbl) with a heating value of 8000 kcal/Nm^3 (900 Btu/scf) is produced from the retort.

Retort products are routed to an accumulator where the solids are passed over a trommel screen to separate the balls from the spent shale. The ceramic balls are recycled to the vertical ball heater by means of a bucket elevator. They are preheated by flue gas coming from the steam superheater. This gas stream also removes shale dust. Emissions are controlled by a wet scrubber. In the ball heater, fuel gas is combusted to heat the balls to 650°C (1200°F).

The spent shale is cooled in a rotating drum steam generator. After cooling, the processed shale is moisturized to approximately 14 percent moisture content in a rotating drum moisturizer. Steam and shale dust produced during the moisturizing step are routed through a venturi scrubber to remove the dust before discharging to the atmosphere. Following moisturizing, the spent shale is conveyed to a disposal site. Dust collected from the various venturi scrubbers is also routed off-site with the processed shale.

Hydrocarbon vapors are routed overhead from the accumulator to a distillation tower. The retort products are normally separated into gas, sour water, naphtha, gas oil and bottom oil streams. A series of parallel operations follows the fractionation as product streams are upgraded and by-products recovered.

A flow diagram of the shale oil upgrading procedure is shown in Figure 2.2-2. Units include gas recovery and treating facilities, naphtha and gas oil hydrotreaters, delayed coker, hydrogen generation unit, water treating facilities, sulfur recovery unit, ammonia separation unit, and steam and electric power generation facilities. Gas from the accumulator is routed to gas recovery and treating and then recycled to the ball heater for combustion or sent to the hydrogen generation unit. The naphtha is normally stabilized and then hydrotreated. The gas oil streams are also hydrotreated. Bottoms oil from the fractionator is thermally cracked by use of a delayed coker to recover additional oil and produce a coke by-product. All H_2S-rich gas streams are routed to the sulfur recovery unit. Wash water from the hydrotreaters is stripped at an ammonia separation unit. Water removed from gas streams is routed to a foul water stripper to remove ammonia and hydrogen sulfide. The stripped water is used for moisturizing spent shale.

Air emission sources for this process are the preheat system, steam superheaters, moisturizing system, process heaters, sulfur recovery unit, crushing and conveying, and power generation. Hydrocarbon storage and fugitive hydrocarbon losses are also included.

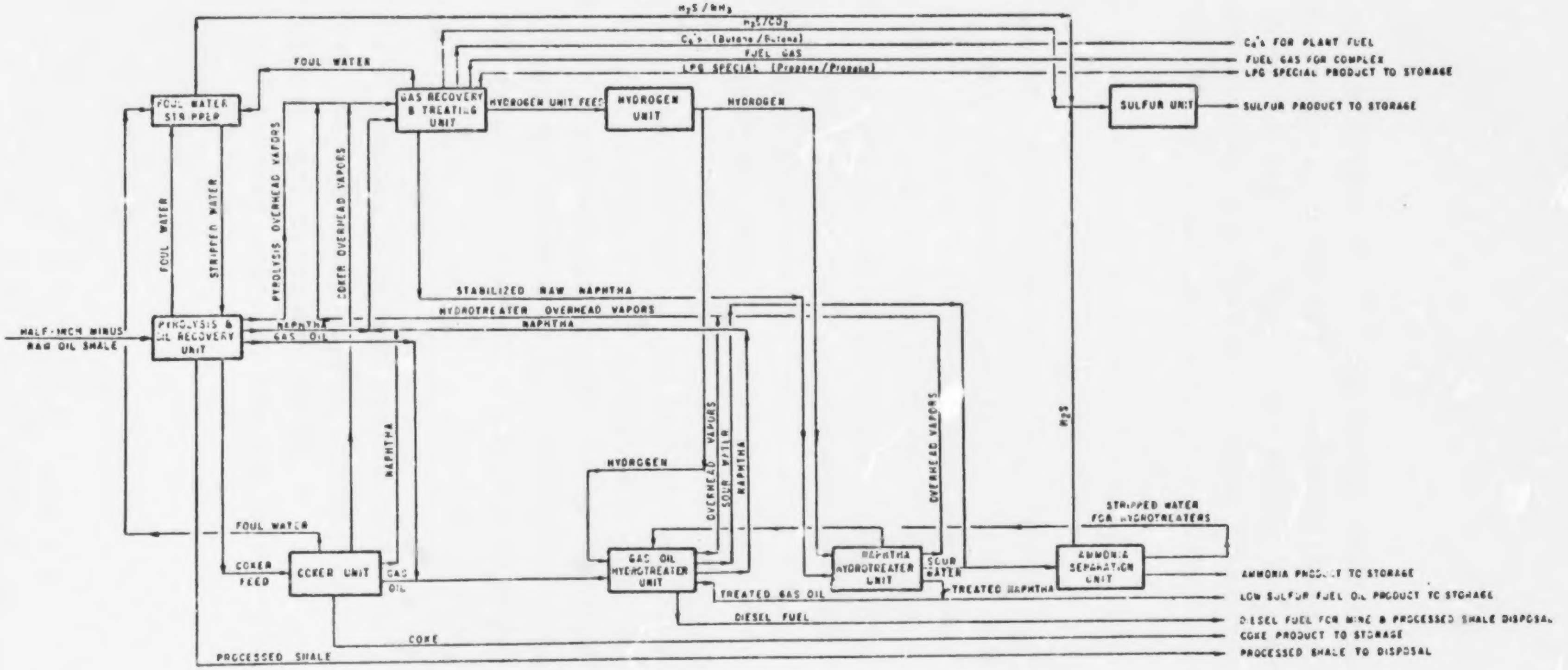

FIGURE 2.2-2 UPGRADING AND BY-PRODUCT RECOVERY FACILITIES

2.2.1.1 Module Basis

Estimates of the emissions are based on an oil shale processing plant producing 7950 m^3/day (50,000 bbl/day) of primary liquid fuels. For an oil shale facility, the primary fuels include naphtha, distillate oil and/or a residual oil. The 7950 m^3/day module was selected since it is the commercial sized facility used for most planning purposes. A feed rate of approximately 59,870 MT/day (66,000 TPD) of raw shale is charged to the retorts. A summary of emissions from an oil shale plant is presented in Table 2.2-4.

2.2.1.2 Module Descriptions

The oil shale processing module for the TOSCO process is comprised of the retorting and shale oil upgrading steps. Raw shale extraction and crushing are not included in this module. The primary fuels from this module are naphtha and fuel oil. The TOSCO II plant at Parachute Creek, Colorado, is designed for raw shale feed of 59,870 MT/day (66,000 TPD). A typical oil shale will contain approximately 12 wt % kerogen or about 146 liters of oil per metric ton of oil shale (35 gal/ton). The resulting primary fuels production will be about 7950 m^3/day (50,000 bbl/day). This represents the anticipated size of a typical oil shale facility associated with an underground mine. Surface mines are anticipated to be capable of supplying shale for a 15,900 m^3/day (100,000 bbl/day) or larger facility.

Processing Steps

The major processing steps for the oil shale module are the following:

1) Retorting,
2) Gas recovery and treating,

TABLE 2.2-4. SUMMARY OF ENVIRONMENTAL IMPACT FROM TOSCO II RETORTING AND UPGRADING MODULE

Basis: 7950 m^3/day Primary Fuels Plant	
Air (kg/day)	
Particulates	7,842
SO_2	3,077
NO_x	16,935
HC	10,607
CO	676
Water (kg/day)	
Suspended Solids	0
Dissolved Solids	0
Organic Material	0
Thermal (kcal/hr)	Negligible
Solid Wastes (MT/day)	49,380
Water Requirements (ℓ/min)	18,263
Energy Recovery Ratio	0.806
Ancillary Energy (kcal/hr)	214×10^6
Manpower Requirements (personnel)	503 - 625

Sources: BA-368, CO-175, HI-083, US-093, US-291

3) Sulfur recovery,
4) Delayed coking,
5) Hydrogen generation,
6) Naphtha hydrotreating
7) Gas oil hydrotreating, and
8) Ammonia separation.

The processing sequence is shown in Figure 2.2-3. In addition to these processing units, support facilities such as utility boilers and water treating facilities are included.

Flow Rates

Module flow rates for oil shale processing are taken from the Colony EIS (CO-175). These rates are as follows:

Raw Shale to Retort - 59,870 MT/day (66,000 TPD)
Spent Shale - 49,380 MT/day (54,430 TPD)
Low Sulfur Fuel Oil - 7,470 m^3/day (47,000 bbl/day)
Liquefied Petroleum Gas - 690 m^3/day (4330 bbl/day)
Ammonia - 122 MT/day (135 TPD)
Sulfur - 157 MT/day (173 TPD)
Coke - 726 MT/day (800 TPD)

Energy Requirements

Energy requirements for this module are given by Colony for the proposed TOSCO II Parachute Creek plant. These heat requirements and fuel mix are shown in Table 2.2-5. The module heat requirements and fuel mix are based on "Mode I" operation.

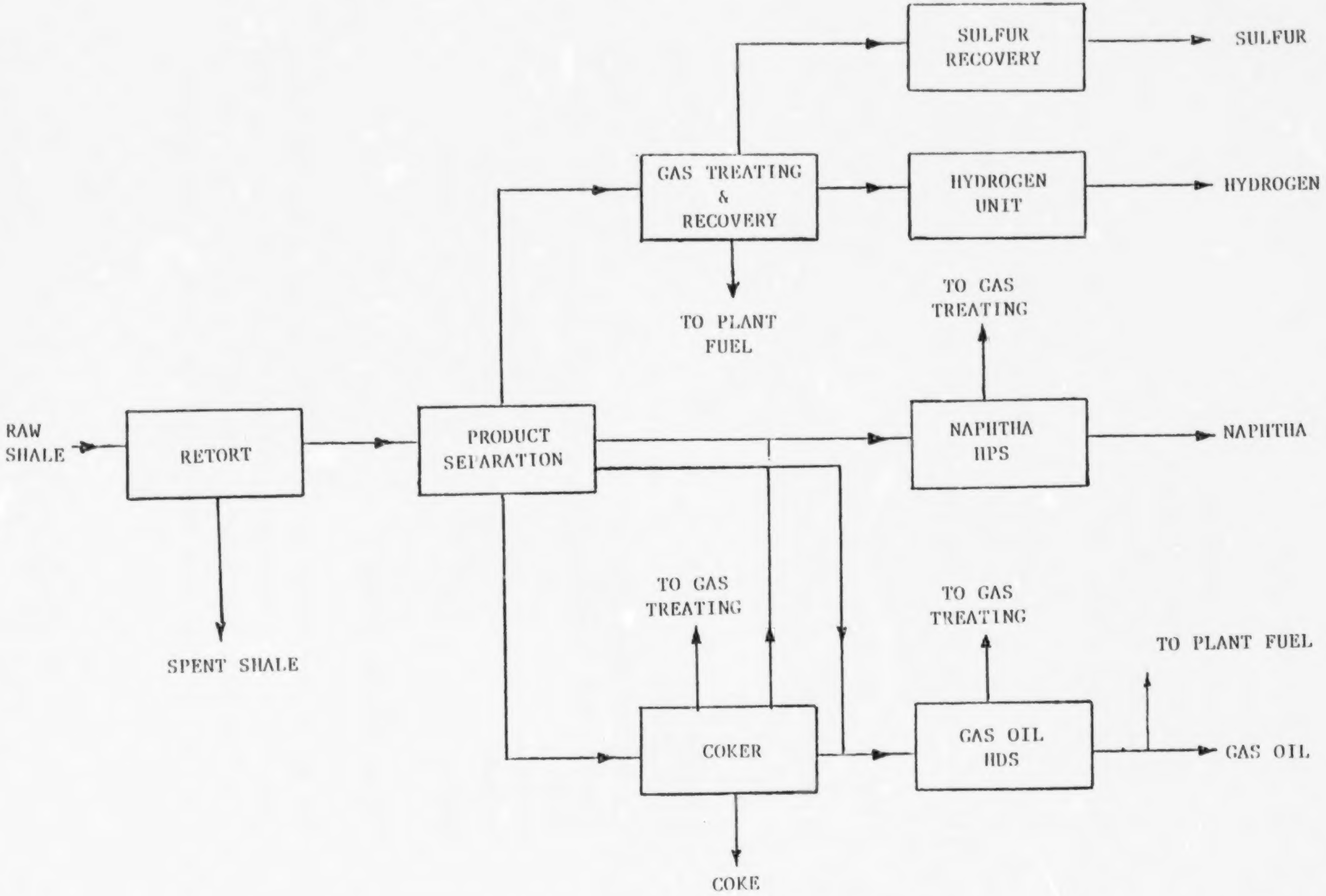

FIGURE 2.2-3 TOSCO II SHALE OIL MODULE

TABLE 2.2-5. PRELIMINARY FUEL BALANCE FOR COMMERCIAL SHALE OIL COMPLEX(1)

	MM BTU/HR					
	Mode I (3)			Mode II (4)		
Source (2)	Fuel Gas	Fuel Oil	C_4 Liquid	Fuel Gas	Fuel Oil	C_4 Liquid
Pyrolysis and Oil Recovery Unit						
Preheat Systems (6)	708	755	384	330	945	307
Steam Superheaters (6)	---	---	144	---	---	120
Hydrogen Unit						
Reforming Furnaces (2)	632	---	---	632	---	---
Gas Oil Hydrogenation Unit						
Reactor Heaters (2)	---	---	47	---	55	---
Reboiler Heater	---	---	40	---	---	48
Naphtha Hydrogenation Unit						
Reactor Heater	10	---	---	11	---	---
Sulfur Recovery Unit						
Sulfur Plants (2) and Common Tail Gas Plant	10	---	---	10	---	---
Delayed Coker Unit	88	---	---	96	---	---
Utilities						
Boilers (2)	---	93	---	---	150	---
Totals	1448	848	615	1079	1150	475

(1) It should be emphasized that while estimates of total fuel consumption are subject to only minor revisions, the allocation of fuels to various sources is quite preliminary, and is not only subject to substantial revision, but will be variable during plant operations.

(2) Where multiple sources are indicated, consumption is for all sources.

(3) Complex is expected to operate in "Mode I" approximately two-thirds of the time.

(4) Complex is expected to operate in "Mode II" approximately one-third of the time.

Source: CO-175

Ancillary energy requirements for the oil shale module are 85,000 kW for the 66,000 TPD TOSCO II operation. Assuming 35% generating efficiency and discounting electrical requirements for mining and crushing, the ancillary energy required is 214 x 10^6 kcal/hr (850 x 10^6 Btu/hr).

The heating values of the fuels are as follows:

Retort gas - 7,253 kcal/Nm^3 (815 Btu/scf)

C_4 Liquid - 11,767 kcal/kg (21,200 Btu/lb)

Distillate Fuel - 9.5 x 10^6 kcal/ℓ (6 x 10^6 Btu/bbl)

Coke - 77,710 kcal/kg (14,400 Btu/lb).

Energy Recovery Ratio

An important consideration for synthetic fuels processing is the efficiency of the conversion from the raw fuel source to a usable fuel. The energy recovery ratio is used as an indication of this efficiency. It is defined as the ratio of the heating value of all the products to the heating value of all the inputs to the module. The heating value of the products includes the net liquid and gas fuels produced along with the coke produced. Sulfur and ammonia are not included. The input heating value includes the gross heating value of the raw shale and the ancillary electrical inputs. The raw shale gross heating value is approximately 2090 kcal/kg (3765 Btu/lb). The energy recovery ratio for the TOSCO II module is calculated as 0.620.

Water Requirements

Water demands of the oil shale industry cannot be accurately defined due to the uncertainty of water requirements for revegetation. Water requirements for this module are based on TOSCO II estimates (CO-175). The water requirements for revegetation are expected to range from 265 ℓ/min (70 gpm) during early development to 2650 ℓ/min (700 gpm) after 12 years. The module water requirements are as follows:

Makeup to Water Treatment for Cooling Tower and Boiler Feed Water Makeup	-	11,563 ℓ/min (3055 gpm)
Makeup to Pyrolysis Unit for Moisturizer and Scrubber losses and Processed Shale Moisturizing	-	3,104 ℓ/min (820 gpm)
Dust Control for Processed Shale	-	946 ℓ/min (250 gpm)
Water for Revegetation	-	2,650 ℓ/min (700 gpm)
Total		18,263 ℓ/min (4825 gpm)

Manpower Requirements

The manpower requirements for the oil shale complex are estimated by Colony (CO-175). The personnel requirements estimated for a commercial oil shale complex are given below:

Administrative	46
By-Products Terminal	8
Processing Area	368 - 470
Disposal Area	73 - 93
Guards	8
	503 - 625

The manpower estimates do not include personnel at the mining facilities. The manpower requirements are assumed to be the same for all the oil shale modules.

2.2.1.3 Module Emissions

The multimedia emissions for oil shale processing are discussed in this section. The EPA criteria pollutants are quantified along with water and solid effluents. The emissions of trace elements and trace organics from oil shale processing are discussed in Section 2.2.4.

Air Emissions

The air emissions in this module result from combustion of fuels, shale moisturizing, sulfur recovery, storage, and miscellaneous hydrocarbon emissions. A summary of module air emissions is presented in Table 2.2-6. This summary represents the most recent update of TOSCO II emissions by Colony Development as presented by Battelle (BA-368). It should be noted that these emission rates differ in some cases from those reported by Colony in the earlier EIA for the plant at Parachute Creek, Colorado. In general, these changes represent the evolution in the plant design.

For example, the revised SO_2 emissions are considerably lower than originally estimated. This is attributed to two factors:

- New Sources Performance Standards were lowered for H_2S in process fuel gas from an anticipated 35 grains H_2S/100 scf to 10 grains/100 scf, which required appropriate design revisions. This would provide a central efficiency of about 99.6%

TABLE 2.2-6. TOSCO II SHALE OIL MODULE (7950 m^3 /day) AIR EMISSIONS AND STACK PARAMETERS

Source	Emissions (kg/day)						Stack Parameters			
	Particulates	SO_2	Total Organics	CO	NO_x	Velocity m/sec	Height m.	Temp. °C	Radius m.	References
1. Pyrolysis & Oil Recovery Unit										
A. Preheat System (6 units)	2,649	555	2,945	447	14,323	15.8	94.6	53	1.42	BA-368
B. Steam Superheaters (6 units)	2,354	1,032	2	31	1,234	14.2	94.6	63	.69	BA-368
C. Shale Moisturizing (6 units)	2,649	-	-	-	-	14.2	94.6	84	.69	BA-368
2. Hydrogen Unit (4 furnaces)	124	257	17	107	895	15.2	24.4	227	.88	BA-368
3. Gas Oil Hydrogenation										
A. Reactor Heater (2 units)	4	10	1	4	29	10.7	22.9	482	.38	BA-368
B. Reboiler Heater	17	41	2	16	122	11.0	45.8	371	.88	BA-368
4. Naphtha Hydrogenation	2	4	1	2	5	7.3	22.9	427	.38	BA-368
5. Delayed Coker	12	30	2	11	92	4.6	53.4	177	1.14	BA-368
6. Utility Boilers (2 units)	31	78	4	28	235	7.6	16.8	204	1.07	BA-368
7. Sulfur Recovery	-	1,010	-	-	-	9.2	64.0	149	1.22	BA-368
8. Refining Misc.	-	-	7,370	-	-	-	1.5	-	-	RA-R-215
9. Storage	-	-	262	-	-	-	15.2	-	-	RA R-215
TOTAL	7,842	3,077	10,607	676	16,935					

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for SO_2 emissions resulting from process fuel gas combustion. In addition, removal efficiencies in the gas treating section for trace organic sulfur compounds, such as mercaptans, were revised.

- Pilot plant data indicates that the preheat section of the Tosco II process can remove SO_2 from flue gas at about 95% efficiency, by the contact of SO_2 with shale dust. This was not taken into account in earlier estimates.

In addition, new nitrogen oxide (NO_x) emission rates are considerably lower than previously estimated. Original estimates assumed that all of the relatively high organic nitrogen content of shale oil was converted to NO_x during combustion in addition to normal NO_x emissions by fixation. Current estimates assume considerably less NO_x formation which is more in line with experimental and published data.

Finally, particulate emissions from the preheat system are reported to be higher than previously indicated. However, this is mostly due to the fact that the new rates reflect total particulates. Total particulates include condensible hydrocarbons as well as solids. Only about half of the reported particulates for the preheat systems are solids.

The air emissions from the module result from several general sources. These sources include fuel combustion, preheating, shale moisturizing, sulfur recovery, petroleum storage, and miscellaneous sources. These sources are discussed below.

Fuel Combustion

Emissions from the combustion of fuels result from the following sources (CO-175):

Pyrolysis or Retorting Unit
Hydrogen Unit
Gas Oil Hydrotreating Unit
Naphtha Hydrotreating Unit
Delayed Coking Unit
Utility Boilers

The type of fuel combusted at the individual sources is determined from the TOSCO II fuel mix (see Table 2.2-Radian used updated emission estimates (BA-368) for these emission sources. In general, these emission rates agree reasonably well with EPA emission factors for combustion sources.

Preheating

Use of flue gas streams for raw shale and circulating ball preheating require additional particulate removal from the flue gas after preheating. Venturi wet scrubbers are used to remove the particulates. It is estimated by mass balance calculations that the Venturi wet scrubber will remove 99.8 percent of the raw shale dust from the flue gas leaving the preheat system and 95.8 percent of the spent shale dust from the flue gas from the steam superheaters leaving the ball circulation system (CO-175).

Shale Moisturizing

The only emissions from the spent shale moisturizing operation are particulates. The emission rates are taken from the updated estimates (BA-368). It is estimated by mass balance calculations that Venturi wet scrubbers will remove 93.0 percent of the spent shale dust. The emission factor for controlled particulate is 0.25 gr/ACF.

Sulfur Recovery

Sulfur dioxide is considered to be the only emission from the sulfur recovery facilities. Sulfur recovery facilities consist of a Claus plant and a tail gas treating unit. Updated emission rates (BA-368) are presented. It is estimated by mass balance calculations that the sulfur recovery facilities will recover 99.7% of sulfur as elemental sulfur. This corresponds to 95 percent sulfur recovery in both the Claus plant and tail gas treating unit.

Petroleum Storage

The following assumptions based on literature, data and experience are formulated to calculate the hydrocarbon emissions from petroleum storage.

1) All product storage is in floating roof tanks.

2) Storage capacity is 10 days (HI-083).

3) Combined hydrocarbon product is equivalent to a crude oil.

Using petroleum storage emission factors for storing crude oil in floating roof tanks (0.029 lb/day - 10^3 gal) hydrocarbon emissions from storage are calculated to be 3.03 g/sec (23.9 lb/hr).

Floating roof tanks will provide approximately 90-95% control of hydrocarbon emissions from storage. These emissions are assumed to occur at a height of 15.2 m (50 feet).

Miscellaneous Sources

There can be numerous miscellaneous hydrocarbon emissions in the shale oil upgrading facilities which escape from sources such as valve stems, flanges, loading racks, equipment leaks, pump seals, sumps, and API separators. These losses are discussed in Radian's Refinery Siting Report (RA-119). Based on literature data, Radian found that the miscellaneous hydrocarbon emissions amount to about 0.1 wt. % of refinery capacity for a new well-designed, well-maintained refinery. This value of 0.1 wt. % is used to determine miscellaneous emissions from the shale oil up-grading facilities. Upgrading capacity is considered to be the feed to the distillation tower (50,000 bbl/day). Crude shale oil from the TOSCO II retort is approximately 21° API (US-093). Hydrocarbon emissions from miscellaneous sources are calculated to be 85.3 g/sec (676 lb/hr). The composition of these hydrocarbons can be expected to be a composite of all volatile intermediate and refined products. The emissions are assumed to occur at a height of 1.5 m (5 feet).

Water Effluents

Water effluents are nonexistent since the module is assumed to operate with zero discharge (HI-083). Any water blowdown streams are routed to containment/evaporation ponds. This wastewater blowdown stream should be high in dissolved solids with some suspended solids and organics. A large amount of water is used on the spent shale pile. The potential exits for runoff from the spent shale pile to leach contaminates from the spent shale. The use and maintenance of a lined catchment basin and containment structure (embankment) will solve this problem.

It has been estimated that, regardless of the quantities of water applied to the surface of the processed shale embankment, infiltration will be limited to the upper two to three feet of the embankment. Runoff water which is to be reused for processed shale disposal should remain in the embankment and is not likely to re-enter surface or subsurface water systems (US-291). This is true as long as the embankments are maintained but may be a problem if the embankments are abandoned.

Thermal Discharge

Thermal discharge to water bodies is zero since no water is discharged from the module.

Solid Wastes

Solid wastes are determined from the amount of spent shale in a typical shale oil process (US-093). This value is 49,380 MT/day (54,430 TPD) of spent shale for a 59,870 MT/day (66,000 tons/day) raw shale process. The geometric mean size of the retorted shale from the TOSCO process is 0.007 cm (.003 in.) with a maximum size of 0.476 cm (0.19 in.) and a minimum size of 0.00077 cm (0.0003 in.) (US-093).

Other solid wastes will be disposed of in the spent shale pile such as water softener sludge and spent catalyst, but these quantities will be very small in comparison to the spent shale. However, the impact may be significant depending on the catalyst and its toxic components if it is disposed in a small area of the embankment and the embankment partially fails.

2.2.2 Paraho Process

The Paraho retort has the capability of using either direct gas combustion (direct mode) or externally heated recycle gas (indirect mode) to achieve the required 480°C (900°F) retorting temperature (PF-003). Publicity releases indicate that recent tests using externally heated recycle gas were considered by Paraho developers to be very successful. This report assesses the Paraho process with externally heated recycle gas.

A vertical retort is used. Coarsely ground shale oil ranging from 1-9 cm (3/8" to 3-1/2") in size is introduced at the top and flows by gravity downward through the retort. Heated recycle gas (or combustion air and recycle gas for direct fired operation) is introduced at several points in the retort, flowing upward countercurrent to the shale. Retorting temperatures reach a maximum of 620-650°C (1150-1200°F). Spent shale is removed from the bottom of the retort. Shale oil vapors leave overhead, passing through an electrostatic precipitator and then to a gas recovery unit. A portion of the noncondensible gas is heated and returned to the retort as recycle gas with the remainder treated for sulfur removal and used in the plant for process fuel. Fuel gas produced by indirect heating usually has a heating value around 7230 kcal/Nm^3 (800 Btu/scf). The Paraho retort is shown in Figure 2.2-4. Upgrading facilities are assumed to be similar to the TOSCO II process.

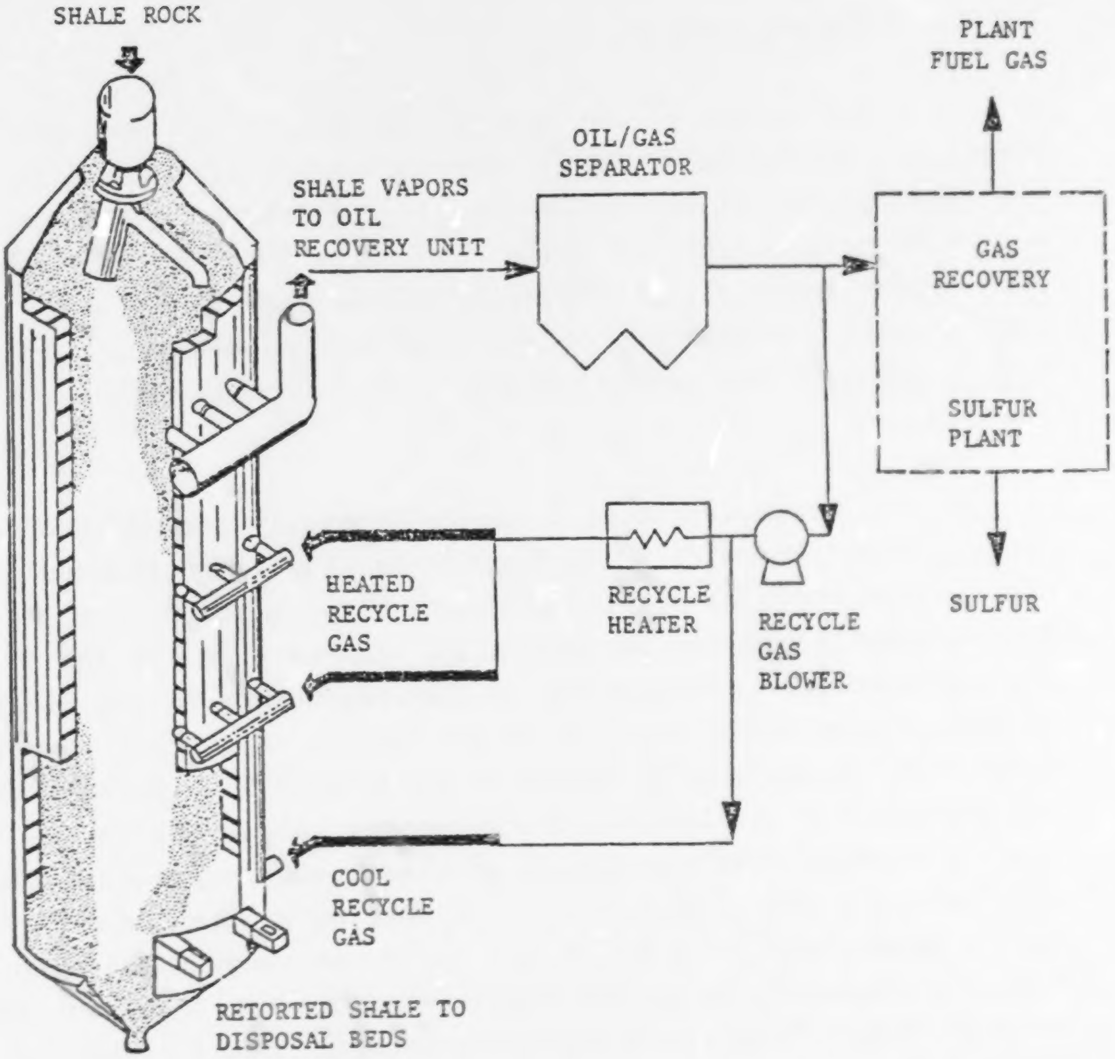


FIGURE 2.2-4. THE PARAHO RETORT PROCESS

2.2.2.1 Module Basis

Estimates of the emissions are based on an oil shale processing plant producing 7950 m^3/day (50,000 bbl/day) of primary liquid fuels. A feed rate of approximately 59,870 MT/day (66,000 TPD) of raw shale is charged to the retorts. A summary of emissions from a Paraho oil shale plant is presented in Table 2.2-7.

2.2.2.2 Module Description

The oil shale processing module for the Paraho process is comprised of the retorting and shale oil upgrading steps. Raw shale extraction and crushing are not included in this module. The primary fuels from this module are naphtha and fuel oil. The Paraho module processes 59,870 MT/day (66,000 tons/day) of raw shale. The raw shale is assumed to contain approximately 30 gallons of oil per ton of oil shale. The resulting primary fuels production will be about 7950 m^3/day (50,000 bbl/day).

Processing Steps

The major processing steps for the Paraho oil shale module are the following:

1) Retorting,
2) Gas recovery and treating,
3) Sulfur recovery,
4) Delayed coking,
5) Hydrogen generation
6) Naphtha hydrotreating,
7) Gas oil hydrotreating, and
8) Ammonia separation.

TABLE 2.2-7. SUMMARY OF ENVIRONMENTAL IMPACT FROM PARAHO RETORTING AND UPGRADING MODULE

Basis: 7950 m^3/day Primary Fuels Plant	
Air (kg/day)	
Particulates	1,178
SO_2	2,734
NO_x	13,785
HC	7,924
CO	593
Water (kg/day)	
Suspended Solids	0
Dissolved Solids	0
Organic Material	0
Thermal (kcal/hr)	Negligible
Solid Wastes (MT/day)	49,380
Water Requirements (ℓ/min)	20,386
Energy Recovery Ratio	NA
Ancillary Energy (kcal/hr)	NA
Manpower Requirements (personnel)	503 - 625

NA = Not Available

The processing sequence is the same as that for the TOSCO II process in Section 2.2.1.2, Figure 2.2-3. In addition to these processing units, support facilities such as utility boilers and water treating facilities are included.

Flow Rates

Module flow rates for the Paraho process are assumed to be very nearly the same as those for the TOSCO II process since both modules assume the same quality raw oil shale and both modules are assumed to operate by indirect heating. The TOSCO II process flow rates are repeated below for the Paraho process.

Raw Shale to Retort	59,870 MT/day	(66,000 TPD)
Spent Shale	49,380 MT/day	(54,430 TPD)
Low Sulfur Fuel Oil	7,470 m^3/day	(47,000 bbl/day)
Liquefied Petroleum Gas	690 m^3/day	(4,330 bbl/day)
Ammonia	122 MT/day	(135 TPD)
Sulfur	157 MT/day	(173 TPD)
Coke	726 MT/day	(800 TPD)

Energy Requirements[1]

Energy requirements for the Paraho module are different than those for the TOSCO II module. The retorting energy requirement can be calculated from the following equation (AT-051):

$$\Delta H_S = A + BT + CT^2 + DT^3 + ET^4 + FT^2G$$

---

[1] Recent information presented by Paraho Development Corporation indicates that the retorting heat requirements may be less than that calculated here (MC-238).

where ΔH_s = enthalpy above 77°F in Btu per pound of shale; T = temperature, °F; G = modified Fischer assay, gallons per ton; A = -52.1723; B = 0.555857; C = -1.15991×10^{-3}; D = 1.68010×10^{-6}; E = -8.15335×10^{-10}; and F = 4.11319×10^{-6}. Assuming a retort temperature of 1150°F for the Paraho process, ΔH_s = 345.5 Btu/lb or 191.5 kcal/kg. This same equation applied to the TOSCO II retort temperature of 900°F gives ΔH_s = 299.4 Btu/lb or 166.2 kcal/kg. When the value for ΔH_s for the Paraho retort is applied to a 7950 m^3/day facility, 507.8×10^6 kcal/hr (2015×10^6 Btu/hr) are required. Consequently, the heat requirements for the Paraho retorting are somewhat higher than that for the TOSCO process.

Ancillary energy requirements for the Paraho process should be lower than those for the TOSCO II process. The Paraho process does not require as much energy for solids handling since raw shale preheating and ceramic ball handling steps are eliminated in the Paraho process. Specific values for the reduced ancillary energy requirements are not available.

Energy Recovery Ratio[1]

As discussed earlier the energy recovery ratio indicates the efficiency of fuel conversion from the raw fuel source. An accurate assessment of the Paraho process energy recovery ratio could not be made because of the lack of available data. However, the energy recovery ratio for the Paraho process may be similar to that of the TOSCO process since the higher retorting heat requirements for the Paraho process tend to be offset by the lower ancillary energy requirements.

---

[1] Recent information presented by Paraho Development Corporation indicates that the energy recovery ratio for the Paraho process is 0.611 (MC-238).

Water Requirements

Water demands for the Paraho process were obtained from Paraho Development Corporation (MC-238). Reported water requirements were for a facility that produced more synthetic crude than the module considered in this report; so their estimates are adjusted accordingly.

Makeup to Pyrolysis Unit	None
Cooling Tower Makeup	10,541 ℓ/min (2,785 gpm)
Solid Residue Disposal	6,756 ℓ/min (1,785 gpm)
Shale Oil Upgrading	3,089 ℓ/min (816 gpm)
Total	20,386 ℓ/min (5,386 gpm)

DEI claims that water requirements for solid residue disposal can be reduced and that shale oil upgrading water requirements can be reduced by upgrading outside the retorting area.

Manpower Requirements

Refer to the manpower requirements for the TOSCO module, Section 2.2.1.2.

2.2.2.3 Module Emissions

The multimedia emissions for the Paraho process are discussed in this section. The EPA criteria pollutants are quantified along with water and solid effluents. The emissions of trace elements and trace organics from oil shale processing are discussed in Section 2.2.4.

Air Emissions

The air emissions in this module result from the combustion of fuels, sulfur recovery, storage, and miscellaneous hydrocarbon emissions. A summary of the module air emissions is presented in Table 2.2-8. This summary assumes that the Paraho process can operate in a similar mode to the TOSCO II process when Paraho uses indirect heating of recycle gas.

The air emissions result from several general sources. These sources are discussed separately in Section 2.2.1.3 and should apply here, except for fuel combustion and preheating.

Fuel Combustion

Emissions from the combustion of fuels result from the following sources:

Pyrolysis or Retorting Unit
Hydrogen Unit
Gas Oil Hydrotreating Unit
Naphtha Hydrotreating Unit
Delayed Coking Unit
Utility Boilers

The modes of operation and, therefore, the combustion emissions for the Paraho process (indirect mode) and the TOSCO II process should be very similar. This is because the heat requirements, the product slate and, consequently, the available fuels are very similar.

Some differences, however, arise in the retorting steps. Because of these differences, the Paraho process emissions for

TABLE 2.2-8. PARAHO SHALE OIL MODULE (7950 m^3/day) AIR EMISSIONS AND STACK PARAMETERS

Source	Emissions (kg/day)					Stack Parameters				
	Particulates	SO_2	Total Organics	CO	NO_x	Rate Nm^3/sec	Height m	Temperature °C	Radius m	Reference
1. Pyrolysis & Oil Recovery Unit	988	1,244	265	425	12,407	635.0	N/A	N/A	N/A	EN-071
2. Hydrogen Unit (4 furnaces)	124	297	17	107	895	85.1	N/A	N/A	N/A	BA-368
3. Gas Oil Hydrogenation										
A. Reactor Heater (2 units)	4	10	1	4	29	3.7	N/A	N/A	N/A	BA-368
B. Reboiler Heater	17	41	2	16	122	12.1	N/A	N/A	N/A	BA-368
4. Naphtha Hydrogenation	2	4	1	2	5	1.4	N/A	N/A	N/A	BA-368
5. Delayed Coker	12	30	2	11	92	12.7	N/A	N/A	N/A	BA-368
6. Utility Boilers (2 units)	31	78	4	28	235	32.5	N/A	N/A	N/A	BA-368
7. Sulfur Recovery	--	1,030	--	--	--	29.1	N/A	N/A	N/A	BA-368
8. Refining Misc.	--	--	7,370	--	--	--	1.5	--	--	RA-R-215
9. Storage	--	--	--	--	--	--	15.2	--	--	RA-R-215
TOTAL	1,178	2,734	7,924	593	13,785					

N/A - Not available. See Table 2.2-6 for these values presented for the TOSCO II process.

pyrolysis were estimated by Radian. The estimate was made by assuming that the same fuels are available to the Paraho process as to the TOSCO II process and then applying emission factors for an industrial heater from AP-42 (EN-071). Exceptions to AP-42 arise for SO_2 and NO_x. For gas combustion, SO_2 was calculated based on 230 Mg/Nm^3 (0.10 gr/scf) of dry H_2S in the fuel gas. Sulfur was assumed to be 0.25 wt % for fuel oil. NO_x emissions from fuel oil combustion was assumed to be 2.16 g $NO_x/10^6$ cal (1.2 lb $NO_x/10^6$ Btu). The SO_2 adjustments conform to new source performance standards (NSPS) for refineries and Colorado regulations. The NO_x adjustments are derived from TOSCO II data for a high nitrogen content fuel.

Preheating

Another difference between the Paraho process and TOSCO II process is that particulate emissions from the Paraho retorting will be significantly less since raw shale preheating, as well as ball circulating and spent shale moisturizing steps are eliminated in the Paraho process. Consequently, particulate control for Paraho retorting is not required.

Water Effluents

Water effluents are nonexistent since the module is assumed to operate with zero discharge (HI-083). Any water blowdown streams are routed to containment/evaporation ponds. This wastewater blowdown stream should be high in dissolved solids with some suspended solids and organics. Impermeable catchment basins and containment structures (embankments) should solve problems associated with runoff from spent shale piles that could potentially discharge leachates to surface or ground waters. Leachates from the processed shale pile to surface and groundwater systems are a potential problem. However, studies indicate that water contamination due to percolation-type leaching will be negligible and that surface leaching will not pose critical problems (US-093). This is true as long as the embankments are maintained but could be a problem if the embankments are abandoned.

Thermal

Thermal discharge to water bodies is zero since no water is discharged from the module.

Solid Wastes

Solid wastes are determined from the amount of spent shale in a typical shale oil process (US-093). This value is 49,380 MT/day (54,430 TPD) of spent shale for 59,870 MT/day (66,000 TPD) raw shale process. The spent shale should be approximately the same size as the charged shale, 1-9 cm (3/8 to 3-1/2 in.). Some of the shale will be crushed as the shale moves downward through the retort and the resulting fines will be entrained in the product gas stream.

Other solid wastes will be disposed of in the spent shale pile such as water softener sludge and spent catalyst, but these quantities will be very small in comparison to the spent shale. However, the impact may be significant depending on the catalyst and its toxic components if it is disposed in a small area of the embankment and the embankment partially fails.

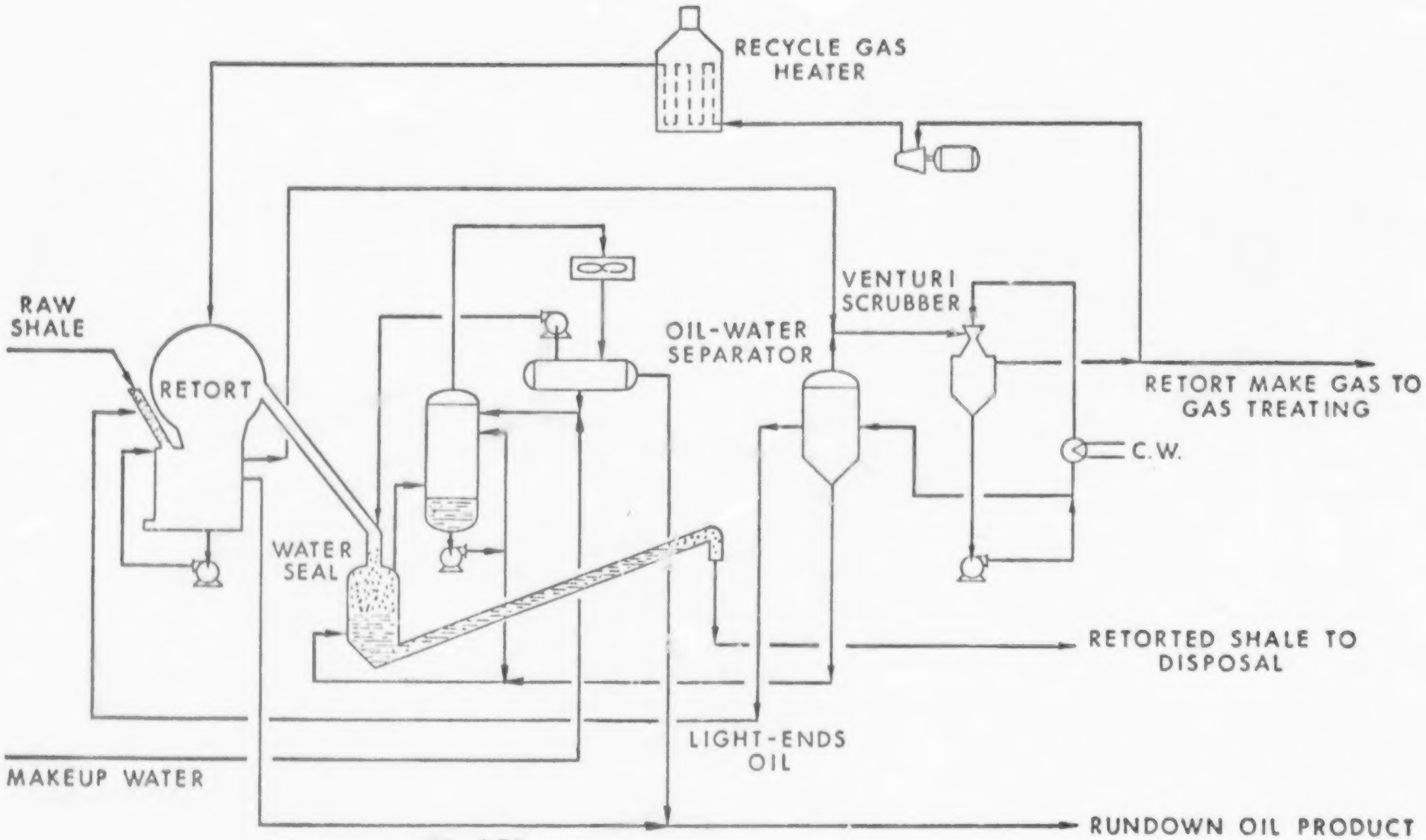
2.2.3 Union Oil Process

In the Union Oil process, oil shale is pumped upward through an expanding cone by a reciprocating piston. A countercurrent stream of hot gas heats the rising bed of shale to the necessary retorting temperature. Retorting takes place near the top of the retort. Oil that is liberated from the shale is carried downward by the gas and gravity toward the cooler shale. This process design reduces agglomeration of the oil shale and the product oil (HO-379).

Union has developed several variations of this basic retorting concept. Retort A, developed in the early 1940's, uses internal combustion to supply heat for retorting. A once through flow of air is heated by the combustion of carbonaceous deposits on the retort shale at the top of the retort. Retort B was developed to produce a higher quality product than Retort A. Retort B uses indirect heat. Recycled product gas is heated indirectly in a furnace to about 510-540°C (950-1000°F). The furnace is fueled by make gas, upgraded product gas, which has a heating value of about 7000 kcal/Nm^3 (800 Btu/scf) (HO-379).

An auxiliary process, SGR (Steam Gas Recirculation), has also been examined by Union. Processed shale from Retort B contains a nominal 4 wt. % carbonaceous deposit. In SGR, the hot processed shale is sent to a separate vessel where the carbonaceous deposit is removed by reacting with steam and air to produce low-Btu gas or with steam and oxygen to produce high-Btu gas. Marginal economics has stopped further work on this process (HO-379). Present plans are to use the Retort B design for development (CL-115). Further discussion in this section is directed at Retort B.

The retorting system using Retort B is presented in Figure 2.2-5. The following description is taken from a report published by the Union Oil Company (HO-379).



Source: HO-379

FIGURE 2.2-5 UNION RETORT B FLOW DIAGRAM

Oil shale from the feed bin flows through two...chutes to the solids pump. Shale oil product acts as a hydraulic seal in the feed chutes to maintain the retort pressure. The solids pump is mounted on a movable carriage ...(and) consists of two piston and cylinder assemblies which alternately feed shale to the retort.

The shale is retorted as it rises through the retort cone. (Heat is supplied by a countercurrent flow of hot recycle gas. As the retorted shale rises above the upper cone lip it forms a freestanding pile.... A rake rotates above...the freestanding pile to break up any agglomerates that may form.

The space above the cone is enclosed by the dome. The (processed) shale slides down chutes and through the dome wall at the (processed) shale outlets. Hot recycle gas is introduced into the space between the (processed) shale pile and the dome. It flows downward into the rising shale to provide the heat required for retorting.... The bulk of the liquid product trickles down through the cool, incoming shale and the balance, in the form of a mist, is carried from the retort by the (cooled) gases. The gas and liquid are separated from the shale in the lower slotted wall section of the retort cone.

The shale particles which fall through the slots into the disengaging section are recycled to the feed chutes. The retorted shale is conveyed in pipes to one of the two retorted shale cooling vessels. As shown in Figure (2.2-5), a level of shale is maintained above the level of water in the quench vessel. A drag-chain conveyor removes the cooled shale from under the water level. A water level is maintained in the conveyor to seal the retort from the atmosphere. Generated steam is condensed and returned to the cooling vessel. The cooled and (moistened) processed shale is sent to disposal.

Gases from the disengaging section are scrubbed and cooled in a venturi scrubber. Agglomerated mist plus light ends and water produced by cooling are sent to an oil-water separator. The oil is recycled to the retort through the oil shale feed line and the water is sent to the water seal after stripping to remove ammonia. The scrubbed gas is divided into a make stream and a recycle stream. The recycle stream is compressed and heated prior to injection into the top of the retort.

The make gas is processed by compression and scrubbing to remove heavy ends and hydrogen sulfide. Oil is used to scrub out the heavy hydrocarbons and Stretford solution is used to remove hydrogen sulfide. The sweetened make gas is used as plant fuel.

The liquid product from the retort is treated sequentially to remove solids, arsenic and light ends. Solids removal is accomplished by two stages of water washing. The shale fines are collected in the water phase which is recycled to the water seal.

The liquid product contains 50 ppm of chemically combined arsenic. (The arsenic concentration is) reduced to about 2 ppm in a proprietary Union Oil process. (The process uses) an absorbent which picks up arsenic to about 80 percent of its weight. About 50 tons of spent absorbent will be placed in the retorted shale disposal area per year. The dearsenited shale oil is sent to a stripping column for stabilization and sweetening prior to upgrading.

Make gas production from the retort will exceed plant fuel requirements. To avoid flaring the excess, the system will be balanced by absorbing the heavy ends of the make gas into the oil product. This will be accomplished by varying the operating conditions of the stripping column and a related debutanizer.

Upgrading facilities are assumed to be similar to the TOSCO II process.

2.2.3.1 Module Basis

Estimates of the emissions are based on an oil shale processing plant producing 7950 m^3/day (50,000 bbl/day) of primary liquid fuels. Specific data for the Union Oil Retort B process was supplied by Union (CL-115) for oil shale containing 142 ℓ/MT (34 gallons/ton). This results in a raw shale requirement of 58,300 MT/day (64,300 TPD), which is slightly lower than the requirement for the TOSCO II and Paraho modules. A summary of the emissions from a Union Oil shale plant is presented in Table 2.2-9.

2.2.3.2 Module Description

The oil shale module for the Union Oil process is comprised of the retorting and shale oil upgrading steps. Raw shale extraction and crushing are not included in this module. The Union Oil module processes 58,300 MT/day (64,300 TPD) of raw shale. The raw shale is assumed to contain approximately 142 liters of oil per metric ton of oil shale (34 gallons/ton). The resulting primary fuels production will be about 7950 m^3/day (50,000 bbl/day).

Processing Steps

The main processing steps involved with the shale oil module are as follows:

1) retorting,
2) gas recovery and treating,
3) sulfur recovery,
4) delayed coking,
5) hydrogen generation,
6) naphtha hydrotreating,

TABLE 2.2-9. SUMMARY OF ENVIRONMENTAL IMPACT FROM UNION OIL RETORTING AND UPGRADING MODULE

(Basis: 7950 m^3/day Primary Fuels Plant)

Air (kg/day)	
Particulates	873
SO_2	1,988
NO_x	8,166
HC	7,984
CO	883
Water (kg/day)	
Suspended Solids	0
Dissolved Solids	0
Organic Material	0
Thermal (kcal/hr)	Negligible
Solid Wastes (MT/day)	48,500
Water Requirements (ℓ/min)	9,840
Energy Recovery Ratio	NA
Ancillary Energy (kcal/hr)	NA
Manpower Requirements (personnel)	503 - 625

NA = Not available

7) gas oil hydrotreating,
8) ammonia separation unit

The processing sequence is shown in Figure 2.2-6. In addition to these processing units, support facilities such as utility boilers and water treating facilities are also included.

Flow Rates

Module flow rates for Union Oil shale oil processing were provided by Union (CL-115). These rates are as follows:

Raw Shale to Retort	58,300 MT/day (64,300 TPD)
Spent Shale	48,500 MT/day (53,500 TPD)
Shale Oil Produced - Net C_5^+	7,950 m^3/day (50,000 bbl/day)
Sulfur	51 MT/day (56 TPD)
Retort Fuel Gas Produced and Consumed - C_4^-	1.64 x 10^6 Nm^3/day (57.9 x 10^6 scf/day)

No estimates were made for ammonia or coke production rates, but they should be similar to the TOSCO II module in Section 2.2.1.2.

Energy Requirements

Energy requirements for Union Retort B are estimated from Union data (CL-115) for the retorting complex alone. Union reports that all of the fuel gas produced at the retort will be consumed in retorting. This amounts to an energy requirement of 438 x 10^6 kcal/hr (1737 x 10^6 Btu/hr). This is slightly more than the energy requirements estimated for TOSCO II process.

Ancillary energy requirements for the Union Oil process are not available. However, the retort charging operation, using

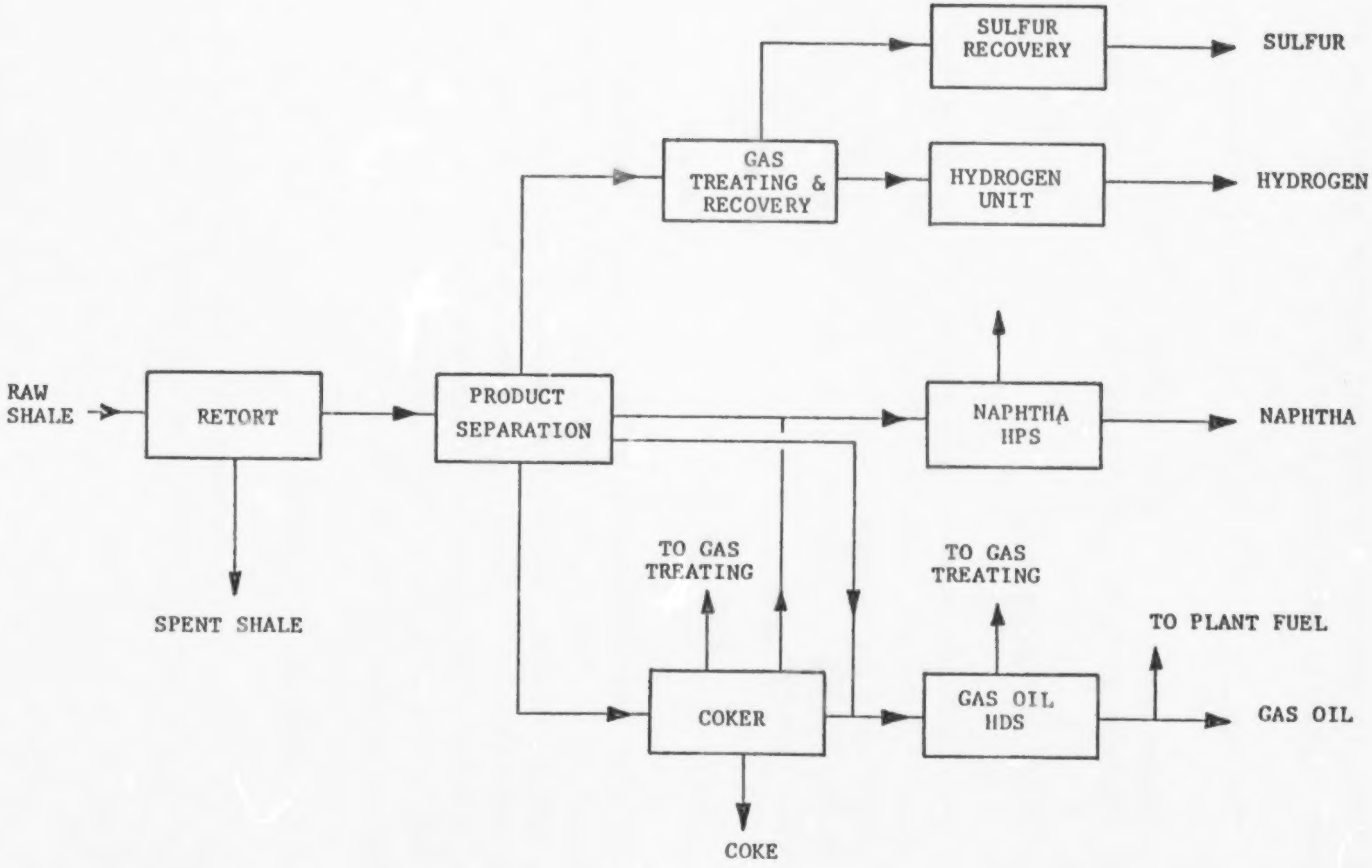


FIGURE 2.2-6 UNION OIL SHALE OIL MODULE

a solids pump, is expected to use much greater quantities of energy than a gravity feed retort (CO-320).

The heating values of the fuels are as follows (CL-115):

Retort Gas	6500 kcal/Nm^3 (720 Btu/scf)
Distillate Fuel	9.5×10^6 kcal/ℓ (6×10^6 Btu/bbl)

Energy Recovery Ratio

As discussed earlier, the energy recovery ratio is an indication of the efficiency of conversion from the raw fuel source. An accurate assessment of the energy recovery ratio for the Union Oil process could not be made because of the lack of available data.

Water Requirements

Water requirements have been estimated by Union (CL-115) for Retort B to be 9840 ℓ/min (2600 gpm). This includes retorting, cooling, gas treatment, deasher, scrubber, processed shale moisturizing and disposal. However, it does not include upgrading and revegetation. The water requirements for Union's Retort B is expected to be similar to TOSCO and Paraho requirements when upgrading and revegetation are included.

Manpower Requirements

The manpower requirements for the Union Oil process are assumed to be the same as those for the TOSCO II process, Section 2.2.1.2.

2.2.3.3 Module Emissions

The multimedia emissions for the Union Oil process are discussed in this section. The EPA criteria pollutants are quantified along with water and solid effluents. The emissions of trace elements and trace organics from oil shale processing are discussed in Section 2.2.4.

Air Emissions

The air emissions in this module result from the combustion of fuels, sulfur recovery, storage, and miscellaenous hydrocarbon emissions. A summary of the module air emissions is presented in Table 2.2-10. This summary presents emissions directly associated with the module operations required to produce the shale oil. The emissions for the pyrolysis and oil recovery unit were provided by Union (CL-115). No data were available from Union on the upgrading facilities; however, operations were assumed to be similar to the TOSCO II process. The resulting emissions should be the same.

The air emissions result from several general sources. These sources are discussed individually in Section 2.2.1.3. All except for fuel combustion and sulfur recovery should apply here.

Fuel Combustion

Emissions from the combustion of fuels result from the following sources:

Pyrolysis or Retorting Unit
Hydrogen Unit
Gas Oil Hydrotreating Unit

TABLE 2.2-10. UNION OIL SHALE OIL MODULE (7950 m^3/day)
AIR EMISSIONS AND STACK PARAMETERS

	Emissions (kg/day)					Stack Parameters				
Source	Particulates	SO_2	Total Organics	CO	NO_x	Rate Nm^3/sec	Height m	Temperature °C	Radius m	Reference
1. Pyrolysis & Oil Recovery Unit	683	1,528	325	715	6,788	N/A	N/A	N/A	N/A	HO-379 CL-115
2. Hydrogen Unit (4 furnaces)	124	297	17	107	895	130.7	N/A	N/A	N/A	EN-071
3. Gas Oil Hydrogenation										
A. Reactor Heater (2 units)	4	10	1	4	29	2.1	N/A	N/A	N/A	EN-071
B. Reboiler Heater	17	41	2	16	122	6.5	N/A	N/A	N/A	EN-071
4. Naphtha Hydrogenation	2	4	1	2	5	0.7	N/A	N/A	N/A	EN-071
5. Delayed Coker	12	30	2	11	92	9.1	N/A	N/A	N/A	EN-071
6. Utility Boilers (2 units)	31	78	4	28	235	20.7	N/A	N/A	N/A	EN-071
7. Sulfur Recovery	--	--	--	--	--	N/A	N/A	N/A	N/A	Radian
8. Refining Misc.	--	--	7,370	---	--	--	1.5	--	--	RA-R-215
9. Storage	--	--	262	--	--	--	15.2	--	--	RA-R-215
TOTAL	873	1,988	7,984	883	8,166					

N/A - Not available. See Table 2.2-5 for these values presented for the TOSCO II process.

Naphtha Hydrotreating Unit
Delayed Coking Unit
Utility Boilers

The air emissions for the pyrolysis or retorting unit are based upon data provided by Union (CL-115) obtained from their pilot plant operations. The emissions result primarily from the combustion of retort fuel gas for heating of recycle gas to the retort. The retorting operations for Union and Paraho processes are similar since they both are assumed to use indirect heating with recycle gas. The primary difference is that Union plans on using only reheat gas for retorting while it is assumed that Paraho is using both retort gas and fuel oil. This will account for some of the differences in retorting emission rates, especially the lower NO_x rate for the Union Retort B.

The upgrading emissions for Union are assumed to be the same as those for TOSCO II. Union reports that they can increase their fuel gas production by changing retort condidtions. It is assumed that they will do this to produce the necessary fuel gas for upgrading heat requirements.

Sulfur Recovery

Union reports that no emissions will be produced at the sulfur recovery unit. Sulfur dioxide is usually considered to be the only emission from the sulfur recovery facilities. However, Union reports that the tail gas from their sulfur recovery unit will be combusted and the SO_2 emissions are accounted for under the pyrolysis and oil recovery unit source.

Union plans on using a Stretford unit for sulfur recovery which should provide a sulfur recovery efficiency of greater than 99 percent.

Water Effluents

Water effluents are nonexistent since the module is assumed to operate with zero discharge (HI-083). Any water blowdown streams are routed to containment/evaporation ponds. This wastewater blowdown stream should be high in dissolved solids with some suspended solids and organics. Impermeable catchment basins and containment structures (embankments) should solve problems associated with runoff from spent shale piles that could potentially discharge leachates to surface or ground waters. Leachates from the processed shale pile to surface and ground water systems are a potential problem. However, studies indicate that water contamination due to percolation-type leaching will be negligible and that surface leaching will not pose critical problems (US-093). This is true as long as the embankment is maintained but may be a problem if the embankment is abandoned.

Thermal

Thermal discharge to water bodies is zero since no water is discharged from the module.

Solid Wastes

Solid wastes are determined from the amount of spent shale in a typical shale oil process (US-093). This value is 48,500 MT/day (53,500 TPD) of spent shale for a 58,300 MT/day (64,300 TPD) raw shale process. The quantity of solid waste for the Union Oil module is less than for the TOSCO II and Paraho modules. This conclusion is solely dependent on the assumption that the Union Oil module uses a higher grade of oil shale. (This assumption is made to correspond with the data supplied by Union (CL-115)). Data is not available on the size of the spent shale.

Spent shale should be roughly the same size as charged shale. The spent shale for the Union Oil process, therefore, should be relatively large in size due to the large size of the charged shale.

Other solid wastes, such as water softener sludge and spent catalyst, will be disposed of in the spent shale site. The quantities of these wastes will be very small in comparison to the spent shale. However, depending on the catalyst and its toxic components, an environmental impact may be significant if the catalyst is disposed of in a small area of the embankment and the embankment partially fails.

2.2.4 Trace Element and Organic Emissions From Oil Shale Processing

Trace elements can be emitted to the environment when oil shale is converted to a synthetic crude oil. Raw oil shale contains trace elements in the form of mineral inclusions or organic complexes. These elements can become part of the emissions and effluents to the environment during oil shale processing, product combustion, or processed oil shale disposal.

Trace organic emissions can also result from oil shale processing. Various organic species are created when kerogen is decomposed in the oil shale retort. These organics can then be emitted during the processing steps or with the disposed processed oil shale.

There is very little information available in the literature concerning trace emissions of elements or organics. Programs are currently underway which are designed to specify the trace emissions from oil shale processing. However, this information is not presently available. This section discusses some of the factors influencing trace emissions from oil shale processing. Available information on oil shale processing and other related processes is used to predict the fate of trace elements and organics during oil shale processing. The discussion is intended to provide only a qualitative description.

2.2.4.1 Trace Elements

Trace elements present in processed Green River oil shale are presented in Table 2.2-11. The same trace elements

TABLE 2.2-11. ELEMENTAL CONCENTRATION OF GREEN RIVER OIL SHALE

Element	Concentration (wt. ppm)	Element	Concentration (wt. ppm)	Element	Concentration (wt. ppm)
Li	850	Zr	9.3	Gd	0.40
Be	35	Nb	3.4	Tb	0.07
B	140	Mo	4.9	Dy	0.40
F	1,700	Ru	< 0.1	Ho	0.07
CI	72	Rh	< 0.1	Er	0.27
Sc	2.4	Pd	< 0.1	Yb	0.25
Ti	570	Ag	< 0.01	Lu	< 0.1
V	29	Cd	0.14	Hf	< 0.1
Cr	49	In	Standard	Ta	0.04
Mn	34	Sn	0.11	W	0.42
Co	39	Sb	0.39	Re	< 0.1
Ni	11	Te	< 0.1	Os	< 0.1
Cu	15	I	< 0.01	Ir	< 0.1
Zn	13	Cs	1.2	Pt	< 0.1
Ga	2.2	Ba	32	Au	< 0.1
Ge	0.40	La	1.4	Hg	< 0.1
As*	7.2 (0.11)	Ce	1.6	TI	0.14
Se	0.08	Pr	0.25	Pb	10.
Br	0.01	Nd	1.2	Bi	0.36
Rb	29	Sm	0.44	Th	0.77
Sr	69	Eu	0.12	U	0.99
Y	1.2				

*Quantity in ( ) is water soluble.

Source: CO-175

are found in the raw oil shale although the concentrations may be different. Very little data on the fate of trace elements in oil shale processing facilities has been published. Atlantic-Richfield has identified 29 elements in a typical Green River shale oil (BU-172).

Experimental Studies of the Fate of Trace Elements in Similar Processes

Recently, attention has been focused on trace element emissions from coal-fired power plants. Coal also contains trace elements that are emitted when the coal is combusted. Certain limited analogies can be drawn between the coal-fired power plant and oil shale processing. Basically, these analogies are:

- both systems handle organic material bound in a matrix with mineral matter, and

- both systems operate at elevated temperatures.

However, this analogy has its limitations. The physical and structural similarities between coal and oil shale are limited. The oil shale retorts operate at lower temperatures than the coal-fired boiler. The coal fed to a power plant encounters an oxidizing atmosphere with the coal combustion products existing in either gas or solid phase; the oil shale fed to a retort encounters a reducing atmosphere. When the Paraho process uses internal combustion, the oil shale is subjected to a reducing atmosphere that contains localized areas of excess oxygen.

In a study of the fate of trace elements in a coal-fired boiler, Radian identified the following elements as being enriched in flue gas (SC-338):

sulfur
mercury
chlorine
antimony
fluorine
selenium
lead
molybdenum
nickel
boron
zinc
cadmium
chromium
copper
cobalt
uranium
arsenic
silver

The following elements exit the stack in the same proportions as in the ash. These include:

barium
beryllium
vanadium
aluminum
calcium
iron
manganese
magnesium
titanium

Based on semiquantitative surveys, tin and germanium are also enriched in the flue gas.

A coal gasifier also has similarities to the oil shale retort. This analogy has most of the similarities and limitations applied to the coal-fired power plant analogy. An additional similarity is that in a gasifier, the coal first encounters a reducing atmosphere and then an oxidizing atmosphere. Gasifiers, however, usually operate at higher pressures than oil shale retorts.

Little work has been published concerning the fate of trace elements in coal gasification systems. Attari (AT-042) has reported some data in connection with the IGT HYGAS pilot plant. The purpose of this work was to measure the concentrations of 11 trace elements found in the solid streams entering and leaving each of the three stages of the HYGAS pilot plant. The HYGAS gasifier section is shown in Figure 2.2-7.

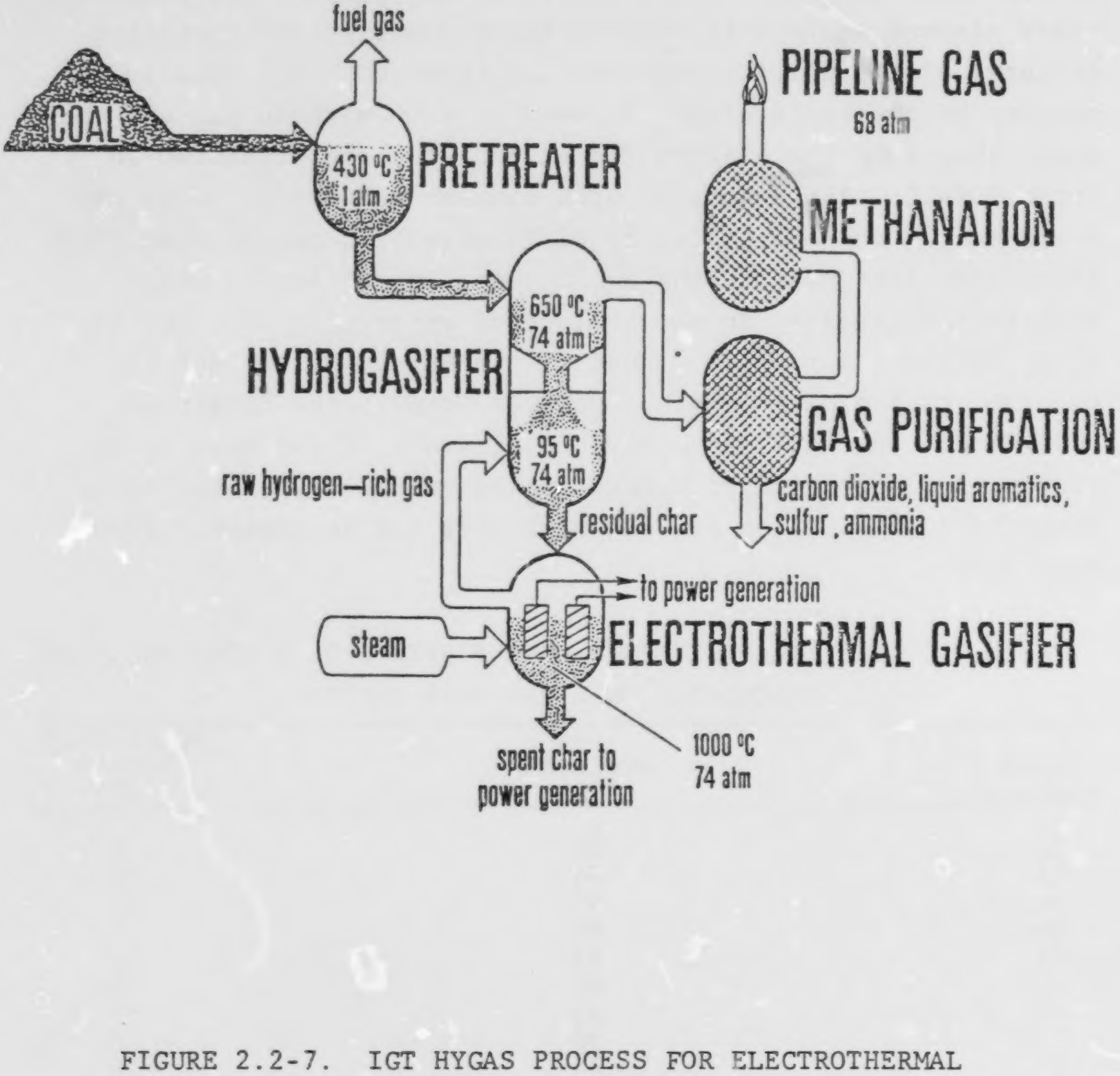


FIGURE 2.2-7. IGT HYGAS PROCESS FOR ELECTROTHERMAL GASIFICATION, SHOWING PRETREATMENT, HYDROGASIFICATION, AND ELECTROTHERMAL STAGES

Because the pilot plant was not operational during the period when the analytical work was performed, coal and char samples accumulated over several years of bench-scale research were used in the analysis. The emphasis of the project was placed on trace element analytical methods since sampling and operating criteria of the pilot plant were not involved. The relative amounts of the trace elements found in the overhead gas and the spent char from the electrothermal gasifier are presented in Table 2.2-12. The amount of each element assumed to be in the overhead gas was calculated by difference. It can be seen from these data that most of the Hg, Se, As, Te, Pb and Cd which entered the gasifier in the coal feed, apparently left the gasifier in the vapor phase. Most of the Sb, V, Ni, Be and Cr remained in the solid phase. However, due to the conditions under which the work was done, the accuracy of the data is in doubt. An indication of trends in the volatility of the trace elements in a gasifier are the best that can be expected from this data.

TABLE 2.2-12. TRACE ELEMENTS CONCENTRATION OF A COAL GASIFIER CALCULATED ON A RAW COAL BASIS

Trace Element	Gas Overhead (%)	Spent Char Bottom (%)
Hg	96	4
Se	74	26
As	65	35
Te	64	36
Pb	63	37
Cd	62	38
Sb	33	67
V	30	70
Ni	24	76
Be	18	82
Cr	0	100

*The % of the trace element in the overhead gas was calculated by difference since only solid analysis was done.

Source: AT-042

Estimation of the Fate of Trace Elements in the TOSCO II Retort

The fate of trace elements in oil shale can be estimated in the TOSCO II retort. Radian has developed a computer program that estimates the composition of a system at chemical equilibrium. The Radian Equilibrium Program is capable of estimating the equilibrium composition of various systems based on the composition of material going into the system and the temperature and pressure of the system. The program is based on the thermodynamic principle that chemical equilibrium is reached when the free energy of the system is minimized. However, there are certain assumptions that limit the validity of the program when it is applied to oil shale systems. These assumptions and their implications are discussed below:

- There are no rate calculations performed in the program. The real system may not actually be at equilibrium, but the program assumes that it is. Discrepancies between the calculated composition of the system and the real composition of the system can result.

- Composition of the kerogen in the raw shale was available (CO-175), but the concentrations of the trace elements was only available for the processed shale (CO-175) (see Table 2.2-11). One source (US-291) states that: "processed shale contains essentially all of the metallic elements found in raw shale." However, the relative concentrations of the trace elements should change as the more volatile elements become depleted in the processed shale. Nevertheless, qualitative trends of the fate of trace elements can be estimated from the processed shale composition. These calculations cannot be considered quantitative.

- The program assumes that all the chemical species are available for reaction. In reality, some of the trace elements may be trapped in the mineral structure. These elements will not contribute to the predicted reactions. This is another reason that the calculations must be considered qualitative, rather than quantitative.

The results of the Radian Equilibrium Program indicate that the following species tend to be enriched in varying degrees in the gas phase of the TOSCO II oil shale retort (the program printout is included in the Appendix).

selenium
cadmium
mercury
boron
germanium
antimony
arsenic
lead
tin

The program also indicates that the following trace elements tend to remain with the processed shale:

beryllium
cobalt
chromium
copper
manganese
molybdenum
nickel
uranium
zinc
barium

The remaining trace elements in the processed shale listed in Table 2.2-11 are not considered by the equilibrium program.

Data Analysis

The fate of the trace elements in the similar processes is compared to the calculated trends for oil shale processing in Table 2.2-13. All of the trace elements predicted to be volatile in oil shale retorting are also volatile in coal-fired boilers and coal gasification. The nonvolatile elements predicted for oil shale retorting that are also nonvolatile in coal-fired boilers are Be, Mn, and Ba. In coal gasification, Be has a low fraction in the vapor phase (18%), all of which may be the result of analytical error.

TABLE 2.2-13. FATE OF TRACE ELEMENTS IN OIL SHALE AND SIMILAR PROCESSES

Trace Element	Oil Shale Retorting (Radian Equilibrium Program)	Coal-Fired Boiler (Radian Data)	Coal Gasifier (IGT HYGAS)
Be	N/V	N/V	V (18%)
Se	V	V	V (74%)
Cd	V	V	V (62%)
Hg	V	V	V (96%)
As	V	V	V (65%)
Pb	V	V	V (63%)
B	V	V	-
Co	N/V	V	-
Cr	N/V	V	N/V (0%)
Cu	N/V	V	-
Ge	V	V	-
Mn	N/V	N/V	-
Mo	N/V	V	-
Ni	N/V	V	V (24%)
Sb	V	V	V (33%)
Sn	V	V	-
U	N/V	V	-
Zn	N/V	V	-
Ba	N/V	N/V	-

V = volatile trace elements
N/V = nonvolatile trace elements

Elements which are predicted nonvolatile in oil shale retorting but volatile in a coal-fired boiler are Co, Cr, Cu, Mo, Ni, U, and Zn. Of this group, Cr is nonvolatile in coal gasification and Ni is only partially vaporized (24%), all of which may also be due to analytical error. No comparisons with coal gasification could be made with Co, Cu, Mo, U and Zn. However, the trend is that elements predicted to be nonvolatile in oil shale retorting also have little or no volatility in a coal gasifier.

The comparisons indicate that the Radian Equilibrium Program predictions for trace elements are reasonable. In addition, analysis of the shale oil by Atlantic-Richfield (BU-172) indicates that arsenic is present in high levels in the synthetic crude. This corresponds with the computer predictions for oil shale processing.

Ultimate Fate of Trace Elements

The volatile trace elements in oil shale will be present in the crude synthetic oil. Many of the elements must be reduced in concentration before the crude is refined. Two general approaches to upgrade raw shale oil are coking and hydrotreating.

The trace elements can be concentrated in the primary fractionation tower bottoms and then fed to a coker where the trace elements are again concentrated in the heavy ends from the coker and on the coke. Arsenic is an exception (BU-172). It cannot be concentrated in a fractionation tower, since it is distributed throughout the entire boiling range. Alternative dearsenation steps are being developed such as irradiation with ultraviolet light and treatment with metal oxides.

The trace elements that remain in the processed shale may be leached by rainfall or snowmelt from shale disposal sites.

Precautions must be taken to prevent drainage from oil shale disposal sites from entering water sources near the site.

2.2.4.2 Trace Organics

Kerogen is the organic polymer contained in oil shale. When heated, kerogen decomposes to yield hydrocarbon gases and liquids. These hydrocarbon products can be processed and refined in much the same manner as petroleum.

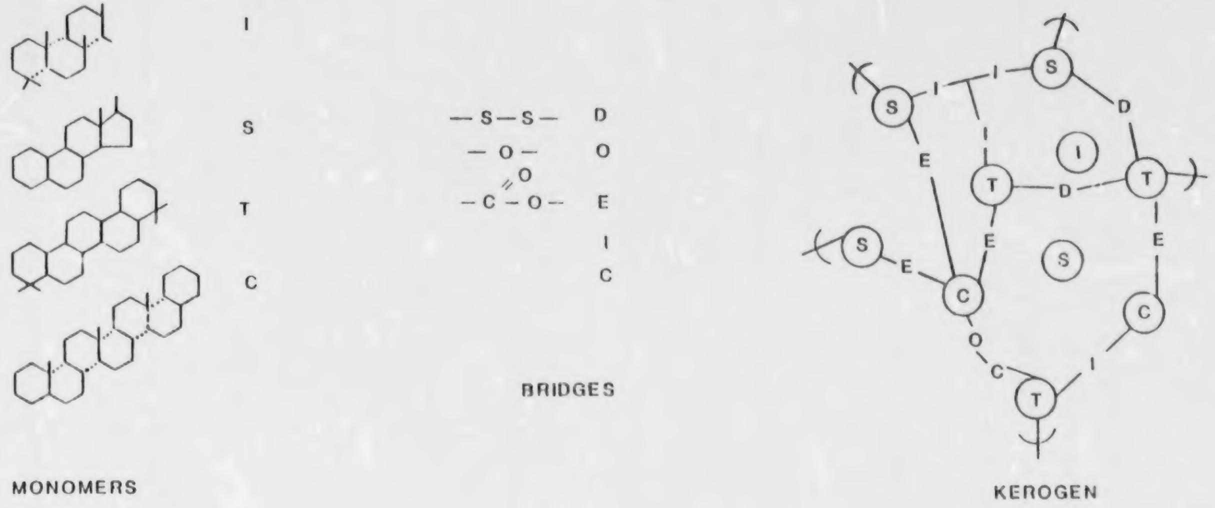
A hypothetical structural model of Green River oil shale kerogen is presented in Figure 2.2-8 (SC-257). From this model it can be seen that five and six carbon rings are basic structures in the kerogen matrix. Also present are disulfides, ethers, and esters. No organic nitrogen compounds are shown although nitrogen is present in rather large quantities. The chemical analysis of kerogen is presented in Table 2.2-14.

TABLE 2.2-14. CHEMICAL ANALYSIS OF KEROGEN

Component	Organic Component, Weight Percent
Carbon	80.52 ± 0.40
Hydrogen	10.30 ± 0.08
Nitrogen	2.39 ± 0.10
Sulfur	1.04 ± 0.08
Oxygen	5.75 ± 0.49

Source: CO-175

Very little information is available concerning the specific components that exist in shale oil. The location and type of oil shale probably affects the composition of the shale oil, since the composition of other fossil fuels, such as crude



The left are the monomers of the multipolymer, kerogen. I, represents isoprenods; T, terpenoids; and C, carotenoids. Bridges can be disulfide (D), ether (O), ester (E), isoprenoid (I), and carotenoid (C) linkages. The entrapped molecules in the matrix of the network are not bonded.

FIGURE 2.2-8 HYPOTHETICAL STRUCTURAL MODEL OF GREEN RIVER OIL SHALE KEROGEN

oil, coal, and natural gas, are dependent upon their location and origin. The type of retort used probably also affects the composition since retorts operate at different temperatures with heat supplied by different mechanisms.

Experimental Studies of the Fate of Trace Organics in Shale Oil Processing

Analogous coal processes which produce organic compounds are coal gasification, liquefaction, coking, and combustion in coal-fired boilers. Very little is known at present on the composition of organics from gasification and liquefaction processes.

Battelle (BA-261) reported forty-two toxic and hazardous organic substances likely to be emitted by industrial boilers (see Table 2.2-15). The organic compounds are listed in order of their decreasing health hazard. The first twelve compounds are all potent carcinogens. This rating is intended only as a guide since a direct comparison of the potency of the various hazardous materials is not always possible.

In a coke plant, cyclic and polycyclic organic matter present in coke oven emissions will be found in the fraction which has been defined as tar. The principal compounds obtained from coal tar as presented by (RO-153) and (MO-125) are given in Tables 2.2-16 and 2.2-17, respectively. Several of the more widely accepted carcinogens are species of benzpyrene. Data resulting from the above samples clearly indicated the presence of benz(c) phenathrene (potent carcinogen), benz(a)anthracene (carcinogen), a benzfluoranthene isomer (possible carcinogen), benz(a)pyrene (potent carcinogen) and/or benz(e)pyrene, and cholanthrene (carcinogen).

TABLE 2.2-15. TOXIC AND HAZARDOUS SUBSTANCES LIKELY TO BE EMITTED BY INDUSTRIAL BOILERS

Organic Materials

7,12-Dimethylbenz(a)anthracene
3-methylcholanthrene
Dibenz(a,h)anthracene
Benz(c)phenanthrene

Benz(a)pyrene
Dibenz(a,h)pyrene
Dibenz(a,i)pyrene
Dibenz(c,g)carbazole

4-Aminobiphenyl
Benzidine
1-Naphthylamine
4-Nitrobiphenyl
Phenylhydrazine

Methyl-phenylhydrazine
Dibenz(a,j)acridine
Dibenz(a,h)acridine
Cholanthrene

Benz(j)fluoranthene
Benz(b)fluoranthene
Dibenz(a)anthracene
Dibenz(a,c)anthracene

Dibenz(a,j)anthracene
Dibenz(a,g)fluorene
Indeno(1,2,3-cd)pyrene
Dibenzo(a,l)pyrene

Benz(a)anthracene
Chrysene
Dibenz(a,c)fluorene
Dibenz(a,h)fluorene

Dibenz(a,i)carbazole
Benz(a)carbazole
Dibenz(c,h)acridine
Picene
Dibenz(a,g)carbazole

Benzoquinoline
Pyridine
Acridine
Aniline

Phenol
Benzthiophenes
Dibenzthiophenes
Thiophene

Source: BA-261

TABLE 2.2-16. PRINCIPAL COMPOUNDS OBTAINED FROM COAL TAR

Hydrocarbons	Nitrogen Compounds	Oxygen Compounds
Naphthalenes	Pyridines	Phenols
Acenaphthene	Quinoline	Cresols
Fluorene	Carbazole	Xylenol
Anthracene	Acridine	Naphthols
Phananthrene	Picoline	
Chrysene		
Pyrene		
Fluoranthene		

Source: RO-153

TABLE 2.2-17. COMPOUNDS OBTAINED FROM COAL TAR

Benzene
Toluene
Xylenes
Phenols
Cresols
Naphthalenes
Anthracene
Phenanthrene
Thiophrene
Thiophene
Pynole
Pyridine
Quinoline

Source: MO-125

The structure of the functional groups in oil shale is similar to that of coal: Both fossil fuels contain groups of six carbon rings fused together. Decomposition of the kerogen in oil shale could result in the production of polycyclic organics as in the coal processes discussed above. Some of these polycyclic organics may be carcinogenic.

The processing of shale oil also has many similarities to crude petroleum refining processes. Indeed, many refinery processes are likely to be used in commercial oil shale processing. It is likely that many of the compounds present in crude oil are also present in shale oil.

Crude oil composition has been studied for many years and analysis is still being done on crude oil fractions. Crude oil contains many organics, some of which are quite toxic in higher concentrations than those usually found in crude oil. Likewise, it is probable that organics in shale oil exist in concentrations below toxic levels. More studies on shale oil composition and toxicity should be conducted to adequately assess the health effects of the components.

Shale oil retorting produces a processed shale containing residual carbonaceous material. The previous discussion has established the possible production of polycyclic organics in oil shale processing. Polycyclic organics have a low volatility. If produced in the process, they will most likely remain with the carbonaceous material on the processed shale.

Studies have been conducted to determine if there is carcinogenic potential in processed shale. These investigations compare the polycyclic organic content in samples of soil, water, vegetation, and air from pristine areas to samples of carbonaceous processed shale from various retorting processes. The samples were analyzed for polynuclear aromatic hydrocarbons (PAH), including those of known carcinogenic properties such as 3,4-benz(a) pyrene.

Preliminary results of these comparisons (SC-257) indicate that the content of benz(a)pyrene (BaP) in benzene extracts of carbonaceous oil shale is about one order of magnitude higher than that in extracts of soil and/or plant material from the pristine environment. Preliminary data also indicates that saline water from leached carbonaceous shale may be at least three to four orders of magnitude higher in PAH content than ground or surface water from pristine areas. It can be concluded that polycyclic organics can be leached from carbonaceous processed shale in the presence of inorganic salts (SC-257). A conclusion of the potential levels of leached PAH has yet to be reached.

The spent shale from high temperature retorts is almost completely free of carbonaceous material. Retorts operating at intermediate temperatures, such as the Paraho process, and lower temperatures, as in the TOSCO II process and Union Retort B, produce a processed shale containing residual organic carbon. These carbonaceous spent shales may contain aza-azarines in addition to PAH (SC-257). Table 2.2-18 lists some compounds identified in carbonaceous spent shale along with the compounds' potential carcinogenicity (SC-239).

Presently, oil shale facilities are planning to design for "zero discharge" of water runoff from processed shale disposal sites. It remains to be seen whether the amount of PAH with carcinogenic properties will constitute a serious hazard to the environment. Additional data is needed along with more experimental studies to determine the impact of the PAH on the environment.

In addition, the effect of atmospheric oxidation of carbonaceous material on exposed processed oil shale needs to be studied.

TABLE 2.2-18. POM* COMPOUNDS IDENTIFIED IN BENZENE EXTRACT OF CARBONACEOUS SHALE COKE FROM GREEN RIVER OIL SHALE

Name of Compound	Potential Carcinogenicity
Phenanthrene	--
Fluoranthene	--
Pyrene	--
Anthanthrene (dibenzo(cdjk)pyrene)	--
Benz(a)anthracene (1,3-Benzanthracene)	+
Benz(a)pyrene	+++
7,12-Dimenthyl(a)anthracene	++++
Perylene	--
Acridine	--
Dibenz(a,j)acridine (1,2-7,8-dibenzacridine)	++
Phenanthridine	?
Carbazole	--

*POM = polynuclear organic matter
+ = high carcinogenic potential
- = low carcinogenic potential

Source: SC-239

BaP Concentrations in Oil Shale Processing Products

Analytical work indicates that processed shale from the TOSCO II process contains less than 40 parts per billion (ppb) of BaP (CO-615). Analysis also shows that the PAH compounds found in processed shale are present in raw shale. Table 2.2-19 presents the BaP content of many common materials found in the environment for comparison (CO-615).

TABLE 2.2-19. BaP CONTENT OF PROCESSED SHALE AND COMMON MATERIALS

Material	BaP (ppb)
Coconut Oil	43.7
Peanut Oil	1.9
Oysters (Norfolk, Va.)	10 to 20
Forest Soil	4 to 8
Farm Field near Moscow	79
Oak Leaves	300 max.
Processed Shale (Colony)	38

Source: CO-615

The BaP content of shale oil is considerably higher than that of processed shale. The BaP concentrations in materials from the TOSCO II process are presented in Table 2.2-20. The concentrations of BaP are given for raw oil shale, processed shale, crude shale oil, hydrotreated shale oil, and shale oil coke (CO-615). Table 2.2-21 shows the BaP content of shale oil compared to other oils (CO-615).

TABLE 2.2-20. BENZ(a)PYRENE CONCENTRATIONS IN OIL SHALE RELATED MATERIALS

Material	Concentration (ppb)
Raw Oil Shale	15*
Processed Oil Shale	30*
Crude Shale Oil	3,130*
Hydrotreated Shale Oil	690
Shale Oil Coke	129

*Samples analyzed at TOSCO and Eppley Laboratories

Source: CO-615

TABLE 2.2-21. BaP CONTENT OF PETROLEUM PRODUCTS

Petroleum Products	BaP (ppb)
Libyan Crude Oil	1,320
Cracked Residuum (API Sample 59)	50,000
Cracked Sidestream (API Sample 2)	2,000
West Texas Paraffin Distillate	3,000
Asphalt	10,000 to 100,000
Raw Shale Oil (Colorado)	3,200
Hydrotreated Shale Oil (0.25% N)	800

Source: CO-615

3.0 COAL GASIFICATION PROCESSING

This section of the report presents a description of coal surface (strip) mining and coal gasification. The Lurgi process is described for production of low-, medium-, and high-Btu gas. Process modules are defined and the impact of the modules is assessed.

3.1 Coal Surface Mining

Coal is one of the most significant of the western energy resources. Proven reserves of coal amount to almost 122 billion metric tons in the western states alone, and total U.S. coal consumption in 1973 was near 0.5 billion metric tons (RA-150).

Most experts believe that if the U.S. is to reach or even approach energy self-sufficiency, the vast coal reserves in the western states must be utilized. The coal found there is characteristically low in sulfur, ash, and Btu content and lies close to the surface in thick seams. It is expected that surface or strip mining techniques will be employed for extracting these reserves. The objective of this section is to provide a description of the processes involved in the surface mining of coal.

Coal Extraction

A surface mine is first opened by making a cut on the thinner overburden side of the coal seam (commonly called the crop line). The valuable topsoil removed from over the coal seam is stored until it can be replaced in areas being reclaimed. The topsoil is usually removed by self-loading scrapers.

After removal and storage of the topsoil, the overburden is prepared for removal. This preparation involves the forming of a smooth working surface called a bench with the stripping machine and bulldozers. The bench matches the width of the pit being dug so the moving vehicles and machinery will have a clear area for moving about.

Upon completion of the bench, a predetermined pattern of holes extending down to near the top of the coal seam are drilled. These blast holes are drilled in a pattern which depends upon the composition and thickness of the overburden. The blast holes themselves are 25 to 40 cm (10 to 15 inches) in diameter. The cuttings from these holes are removed by compressed air, collected by a cyclone dust collection system built into the drills, and deposited on the ground near the hole. After placement of the explosive, the cuttings are used to backfill the hole.

Following the drilling the holes are charged with explosives. The size of the charge injected depends upon the materials encountered in the overburden, the locations of the various strata to be blasted, the spacing of the adjacent holes, and the total depth of overburden.

When the charges have been set and all equipment moved to a safe location, the holes are connected for detonation by a detonating fuse and/or electric blasting caps. A delay connector insures proper detonation. It provides the best fregmentation of the coal with minimal vibration and dust generation.

Once the overburden has been blasted, it is ready for removal. Long-reach electric- or diesel-powered draglines are commonly used as the overburden removal tool. Alternatively, a mine may use diesel powered shovels. The dragline positions itself on the bench for removal of the overburden. It then proceeds parallel with and down toward the coal seam. Simultaneously, the dragline and bulldozers are constructing a bench to replace the one being removed. The cycle continues until the overburden thickness reaches an economic or physical limit.

After overburden removal, the surface of the coal seam is cleaned of any material left with a bulldozer. Should the coal need to be fractured prior to loading, a grid of blast holes is drilled into the seam. Charges are detonated and fracture the coal in planes, allowing easy digging and loading with minimal coal dust emissions.

The loading of the cleaned and possibly fractured coal is the next step in surface mining. Loading is often accomplished with a large electrically-powered shovel. An articulated front end loader is used for support and clean-up work. Typically, the coal is loaded directly into large off-highway-type trucks. These trucks usually discharge their load directly into hoppers which feed via conveyors directly to the crushing and sizing plant.

Coal Sizing

Coal preparation facilities are designed to provide properly sized coal to the plant gasifier. Preparation operations also generate coal fines which cannot be fed into the Lurgi gasifier and are consequently sold, gasified in a small Lurgi gasifier to produce plant fuel, or burned in the plant boilers. A number of facilities are included in the preparation operation. These are run-of-mine coal unloading, primary crushing, primary screening, secondary crushing and screening, coal storage, reclaiming, coal fines cleaning, and associated belt conveyors.

The run-of-mine coal is usually hauled by truck, conveyor, or rail to hoppers which feed into the coal preparation area. Here the coal is crushed and screened to a minus 5 cm product. Oversize coal goes to a secondary crusher where it is reduced to a minus 5 cm product. Crushing and screening operations can be performed either at the mine site or at the gasifier plant site.

The sized coal from the primary and secondary crushing operations is next loaded on a belt conveyor. This conveyor transports the coal to storage stock piles.

Coal from the stock piles is transported by covered conveyors to active storage bins. These bins are designed for two or more days' storage capacity and serve primarily as surge capacity. Active storage bins are covered and equipped with dust collectors.

In preparation for emergencies a large supply of coal is set aside in dead storage. This coal pile is prepared on an impermeable base. As a guard against wind and water erosion and the resulting pollution, dead storage piles may be sprayed with asphalt or polymer crusting agents (BU-087, FA-084, MA-294).

From the storage bins, the coal is transported to a screening arrangement which sorts the coal into three sizes:

1) minus 5 cm to 1 cm,
2) minus 1 cm to 2 mm, and
3) smaller than 2 mm (fines).

The first two categories are fed separately into the Lurgi gasifier while the coal fines are cleaned for use in the plant boilers. Excess fines go to sales or gasification.

3.1.1 Module Basis

The coal strip mining module is based upon an operation capable of supplying sufficient amounts of sized coal for a high-Btu Lurgi coal gasification complex producing 8.2×10^6 Nm^3/day of SNG (288 MMscfd). The required output for the module is 25,600 metric tons/day of coal (28,000 TPD). A summary of the environmental impact from the mining and sizing operations is presented in Table 3.1-1.

TABLE 3.1-1. SUMMARY OF ENVIRONMENTAL IMPACT FROM COAL STRIP MINING

Basis: 25,600 MT/day (28,000 TPD) of coal	
Air (kg/day)	
Particulates	3794
SO_2	83
NO_x	1125
HC	130
CO	676
Water Effluents	0
Thermal	neg
Solid Wastes (MT/yr)	15.6×10^6
Ancillary Energy (kcal/hr)	1.84×10^7
Energy Recovery Ratio	0.997

3.1.2 Module Description

The basic steps involved in area stripping operations are shown in Figure 3.1-1.

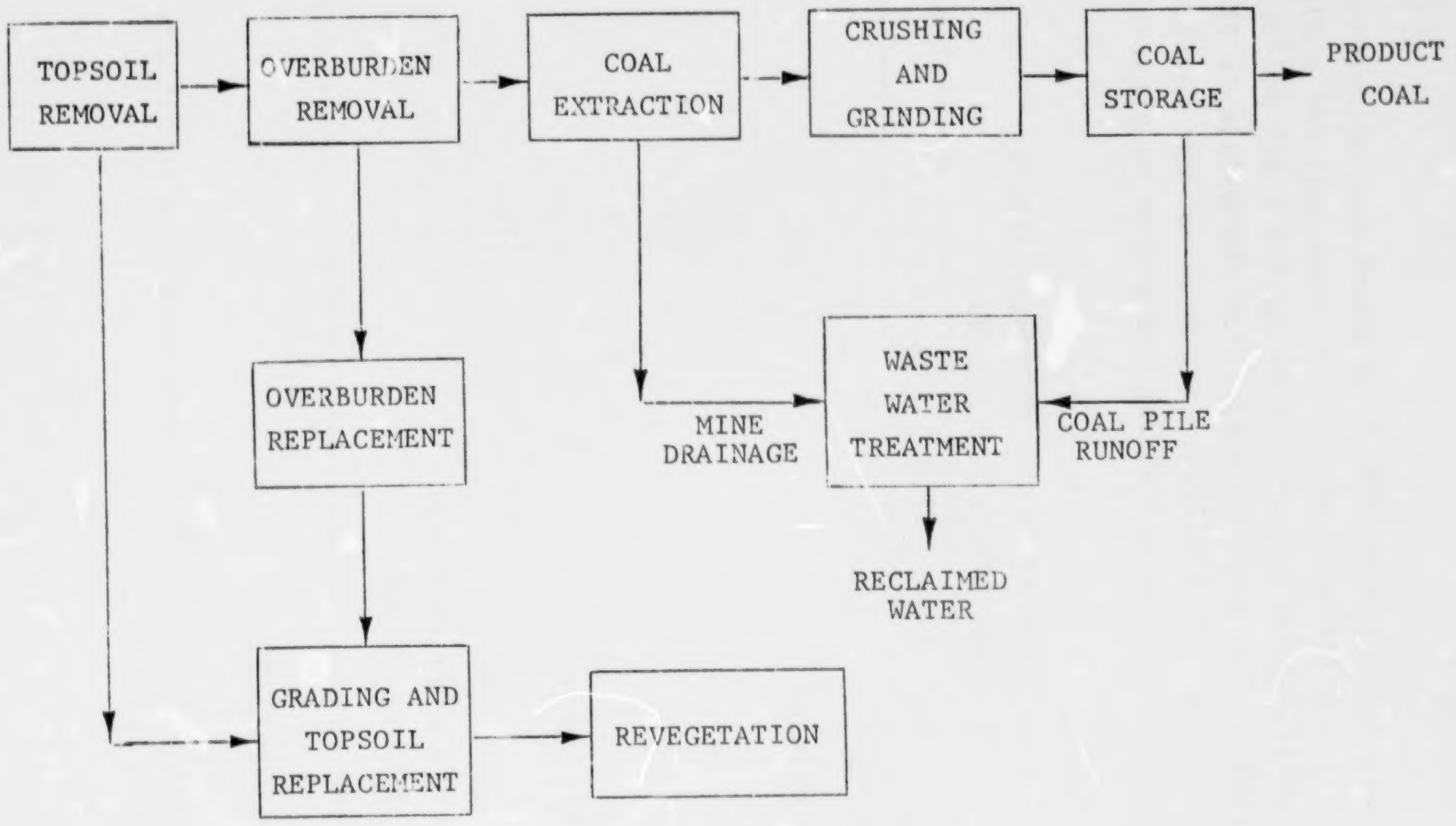


FIGURE 3.1-1 STEPS INVOLVED IN AREA STRIPPING OPERATION

Topsoil and overburden are first removed and placed in separate storage areas. After the exposed coal seam is mined, overburden and topsoil are replaced and reclamation activities begin. In an established strip mine, mining and reclamation activities take place on a simultaneous, continuous basis.

In addition to the mine site operations just mentioned, major facilities found at a typical strip mine include haulage roads, run-off water collection and treatment facilities, and a crushing and sizing plant. In this study, the mining module is assumed to include all the steps necessary to prepare coal for subsequent processing in a Lurgi gasification complex.

Flow Rates

Coal facilities in the mine and sizing area handle an average of 25,680 MT/day (28,250 TPD) of sized coal. During the crushing and screening operations coal fines are formed and separated at the rate of approximately 9,000 MT/day (9900 TPD) (WY-007). These fines are cleaned and sold. The total amount of coal mined daily is therefore about 34,680 metric tons (38,150 TPD).

Energy Requirements

The energy requirements for this module are summarized on Table 3.1-2. The numbers were derived from a Hittman Associates report (HI-083). The estimates are based on a hypothetical surface mine in the Powder River Basin.

TABLE 3.1-2. DAILY ENERGY REQUIREMENTS FOR WESTERN COAL SURFACE MINING

Operation	Electricity (kWh)	Diesel Fuel (ℓ)	Total (kcal)
Mining	0.63×10^5	16,039	2.2×10^8
Hauling		3,503	$.3 \times 10^8$
Crushing	1.20×10^5	5,730	1.9×10^8
Reclamation		150	$.02 \times 10^8$
Total	1.83×10^5	25,422	4.42×10^8

Energy Recovery Ratio

The energy recovery ratio for this module was determined by dividing the total heating value of the coal produced (34,680 metric tons/day or 1.67×10^{11} kcal/day) by the sum of this number and the module energy requirement. The energy recovery ratio for this module is 0.997.

Water Requirements

The only process water requirements for the mining module consist of the water used for dust control in the sizing operations and along haulage roads. El Paso Natural Gas estimates that about 6.54×10^6 ℓ/day (1200 gpm) of water is needed for a mine this size (US-112).

3.1.3 Module Emissions

This section presents the environmental impacts of coal surface mining. Air, water, and solids emissions are discussed and estimated using information from the Environmental Assessment (WY-007) for the Wyoming Coal Gas and Rochelle Coal Company coal gasification project.

Air Emissions

Major sources of air emissions found within a typical strip mining operation include:

extraction operations,
coal sizing,
ash handling, and
reclamation.

Table 3.1-3 presents the atmospheric emission estimates for this module. The use of emission control equipment was not assumed in calculating these estimates.

TABLE 3.1-3. ATMOSPHERIC EMISSIONS FROM COAL SURFACE MINING

Basis: 34,680 MT/day (38,150 TPD) coal mined

	Emissions (kg/day)				
	Part	SO_2	NO_x	HC	CO
Wind erosion	190				
Overburden excavation	1500				
Ash handling and disposal	500				
Blasting of overburden	374				
Mining roads	320				
Blasting of coal	40				
Drilling	50				
Topsoil removal and storage losses	25				
Coal crushing, screening, loading, sizing, and conveying	750				
Diesel equipment	45	83	1125	130	676
Total	3794	83	1125	130	676

Extraction Operation

The dust generated from the various extraction activities is the major atmospheric emitter in this module. SERNCO reports that approximately 120 acres per year for a typical operation are disturbed due to surface mining operations (WY-007).

Blast hole preparation by drilling releases noticeable amounts of particulates. For a surface mine producing similar rates of coal as this module, SERNCO (WY-007) estimates that up to 50 kg/day (110 lb/day) of particulates are discharged from the drilling of blast holes. The blasting of the overburden injects a considerable amount of dirt and dust into the atmosphere, but this operation occurs only periodically. SERNCO estimates that blasting emits 374 kg/day (824 lb/day) of particulates less than 10μ in diameter. Larger diameter particules are assumed to settle out in the immediate vicinity of the mine.

The fugitive dust emitted during the removal of the overburden is the main source of particulates in a coal surface mine. For this phase of mining, SERNCO estimates that roughly 0.035 kg of dust is discharged per metric ton of overburden moved. Assuming 15.6 x 10^6 MT per year of overburden is removed (WY-007), this results in particulate emissions of approximately 1500 kg/day (3000 lb/day). Some dust is also released in the shooting of the coal. SERNCO estimates these emissions to be about 40 kg/day. Another source of fugitive dust is wind erosion. Based on an equation developed by PEDCo-Environmental for estimating these losses, a daily emission of 190 kg (420 lb) of particulates is calculated (CO-352).

Hauling the coal on mine roads will result in the dispersion of dust from both payloads and road surfaces. SERNCO estimates that 320 kg/day (705 lb/day) of particulates result from coal hauling.

The removal of topsoil and its storage prior to mining is another source of dust in this module. It is estimated by SERNCO that this operation discharges 25 kg/day (55 lb/day) of dust to the atmosphere. Wetting of the topsoil to reduce emissions is not planned.

The diesel-powered equipment constitute a major source of emissions. This equipment consumes approximately 25,400 liters of fuel (6,700 gal) each day according to Table 3.1-2. The total estimated daily emissions from all equipment for this module is summarized in Table 3.1-4. The emission factors used were for heavy-duty diesel vehicles (EN-071).

TABLE 3.1-4. ATMOSPHERIC EMISSIONS FROM DIESEL-POWERED EQUIPMENT

Pollutant	Emission Rate (kg/day)
Particulates	37
SO_2[1]	83
NO_x	1125
HC	130
CO	676

[1] Based on average sulfur content for diesel fuel of 0.2 percent.

Coal Sizing

The crushing, sizing, screening, and conveying activities result in the discharge of a moderate amount of dust. From these operations greater emissions may occur during the dry, hot, summer months. SERNCO estimates that 0.025 kg of dust are emitted per metric ton of coal crushed, screened, sized, and conveyed

(WY-007). Therefore, approximately 750 kg/day (1650 lb/day) of particulates are emitted from this module. These operations will be covered to aid in reducing dust emissions. No other controls are planned.

Ash Handling

The short-haul transportation of gasifier ash from the plant back to the mine generates a small amount of fugitive dust. These emissions are minimal since the ash is wet. SERNCO estimates that this operation results in particulate emissions of 500 kg/day (1100 lb/day). Since the material is hauled wet, no dust controls are planned.

Liquid Effluents

All mine drainage and surface run-off is assumed to be collected, treated, and used to satisfy mine site water demands (dust suppression). Therefore, no liquid effluent streams are anticipated. Since no water effluents are assumed, thermal discharges are negligible.

Solid Wastes

The mine overburden must be disposed of at a rate of 15.6 x 10^6 MT per year. This quantity represents the solid waste generation rate of this module.

3.2 Coal Gasification

The gasification of coal to form a low-, medium-, or high-Btu synthetic gas is one means of supplying the demand for natural gas. Many coal gasification projects have been proposed with several scheduled to begin construction in the near future.

Technology has been available since the mid-1800's for the production of a low-Btu gas from coal. The process studied in this report was successfully proven on a pilot scale in 1930. A. Cr. Saechsische Werke built this pilot plant at Hirschfelds, Germany. Werke's process was the forerunner of the Lurgi process which was developed by Lurgi Mineraloltechnik, GmbH, a West German company. This is still the only commercially successful high-pressure technique for producing a low-Btu gas from coal. As of 1974, sixteen plants have applied this technology (US-112). These plants have produced town gas or low-Btu gas. Almost sixty grades of coal, including coke, anthracite, semi-anthracite, bituminous and subbituminous coals, coking coals, lignite, and peat have been successfully processed.

Currently no commercial scale facility exists which produces high-Btu gas. A number of methanation pilot plants and a demonstration plant in Scotland, though, have produced a high-Btu gas from Lurgi synthesis gas.

The objective of this section is to provide a description of the processes of producing low-, medium-, and high-Btu synthetic gas using Lurgi technology. A discussion of the high-Btu Lurgi gasification process is followed by a discussion of the low- and medium-Btu Lurgi gasification processes.

3.2.1 High-Btu Lurgi Gasification

High-Btu coal gasification produces a synthetic natural gas (SNG) with a heating value of 8400 to 8900 kcal/Nm^3 (950 to 1000 Btu/scf). Figure 3.2-1 shows a simplified flow diagram of the major steps in Lurgi high-Btu gasification. The following paragraphs provide a brief description of the process steps.

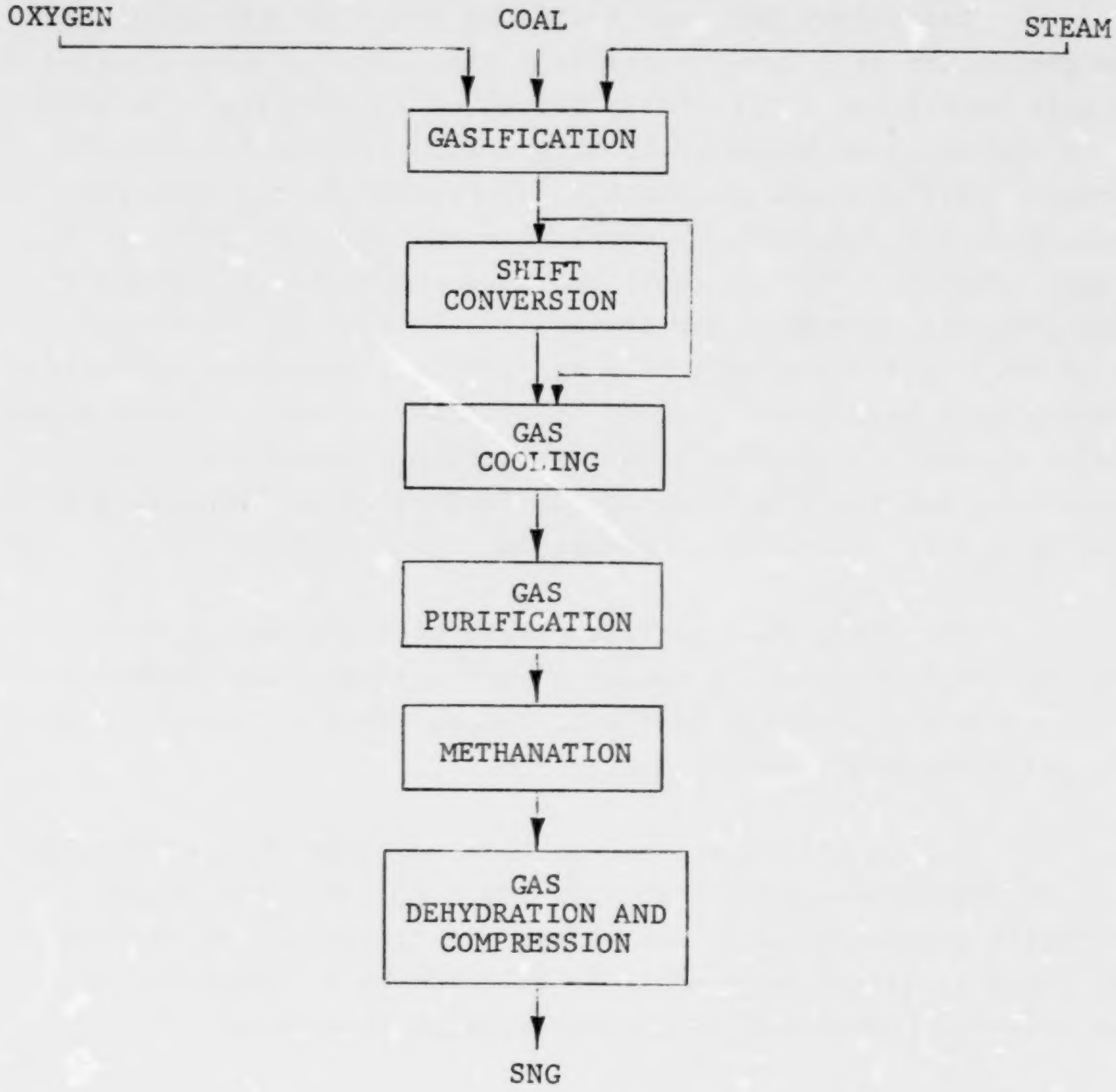


FIGURE 3.2-1 GENERAL FLOW DIAGRAM OF LURGI HIGH-BTU GASIFICATION

Gasification

Figure 3.2-2 shows a diagram of the Lurgi gasifier. Coal is fed intermittently into the gasifier via a coal pressure lock. As the coal travels slowly downward, it contacts a hot rising stream of synthesis gas and is heated to 370 to 590°C (698 - 1094°F). This heating causes the coal to be successively dried, devolatilized, and gasified. Coal undergoes devolatilization according to Equation 3-1:

$$\text{Coal} + \text{Heat} \rightarrow C + CH_4 + \text{Organics} \qquad (3\text{-}1)$$

The devolatilized coal reacts further with the rising hot synthesis gas in the gasification zone of the gasifier according to Equations 3-2 and 3-3:

$$C + 2H_2 \rightleftarrows CH_4 + \text{Heat} \qquad (3\text{-}2)$$

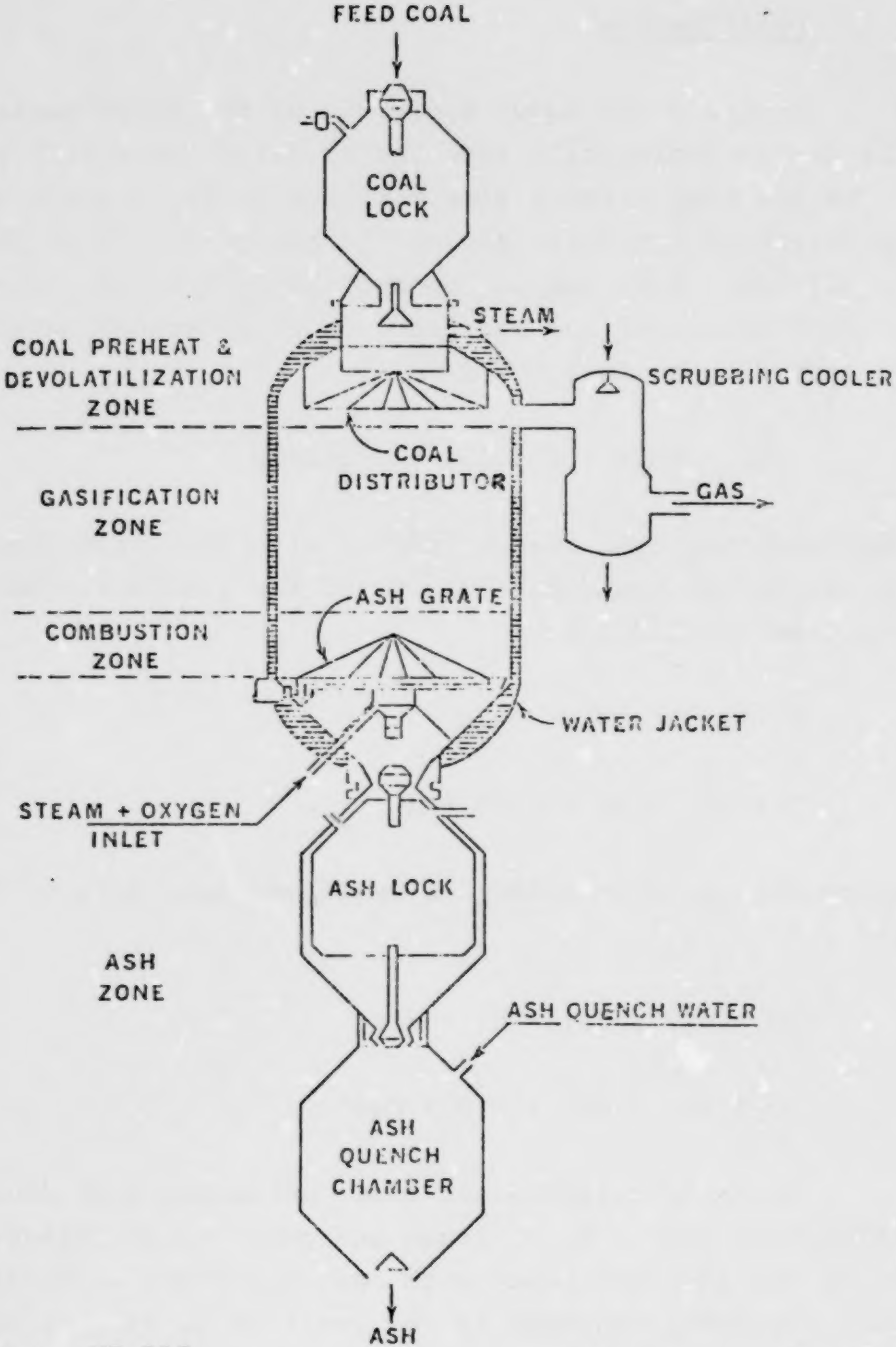
$$C + H_2O + \text{Heat} \rightleftarrows CO + H_2 \qquad (3\text{-}3)$$

The synthesis gas also undergoes reactions according to Equations 3-4 and 3-5:

$$CO + H_2O \rightleftarrows CO_2 + H_2 + \text{Heat} \qquad (3\text{-}4)$$

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O + \text{Heat} \qquad (3\text{-}5)$$

From the gasification zone, unreacted coal descends to the combustion zone. Here, steam and pure oxygen injected at the bottom of the gasifier react with coal according to Equations 3-3 and 3-6, supplying the heat to the gasifier as well as the synthesis gas required in the gasification and devolatilization zones:



Source: US-112

FIGURE 3.2-2 THE LURGI GASIFIER

$$C + H_2O + \text{Heat} \rightleftarrows CO + H_2 \qquad (3\text{-}3)$$

$$C + \tfrac{1}{2}O_2 \rightleftarrows CO + \text{Heat} \qquad (3\text{-}6)$$

A revolving ash grate at the bottom of the combustion zone supports the coal bed and also distributes the steam and oxygen or air fed to the gasifier. The grate also allows for removal of ash. The ash exits the gasifier via lock hoppers and is water quenched. It is then sent to a dewatering area. Steam is used to pressurize the ash lock hoppers so that no gases will be emitted to the atmosphere when the ash is released from the locks.

A raw synthesis gas (see Table 3.2-1) composed mainly of CO, CO_2, H_2, CH_4 and steam (also N_2 if the low-Btu gasification scheme is used) is removed from the top of the gasification zone. The gas is scrubbed with water to remove entrained particulates and to condense heavy hydrocarbons.

Shift Conversion

In the high-Btu scheme the raw gas which leaves the gasification section is split into two approximately equal streams, one feeding into the gas cooling area and the other directed to the shift conversion area. The primary function of the shift conversion operation is to adjust the H_2/CO mole ratio of the mixed gas stream to 3.5 to 1 to optimize the methanation step. The shift conversion is accomplished in a catalytic, adiabatic water gas shift reactor via Equation 3-7:

$$CO + H_2O \rightleftarrows CO_2 + H + \text{Heat} \qquad (3\text{-}7)$$

The operating conditions and catalyst are designed to allow this conversion to take place in the presence of heavy hydrocarbons, tar oils, sulfur compounds, and naphtha.

TABLE 3.2-1. SYNTHESIS GAS COMPOSITION FOR AN OXYGEN BLOWN LURGI GASIFIER

Component	Volume Percent (Dry Basis)
CO_2	28.4
H_2S	0.5
CO	19.9
H_2	38.7
N_2 + Air	10.3
CH_4	0.3
C_2H_4	0.1
C_2H_6	0.6
C_3H_6	0.2
C_3H_8	
C_4H_8	
C_4H_{10}	

Source: US-349

Gas Cooling

The gas is cooled by generating low-pressure steam in a waste heat recovery unit. The crude gas is cooled once more in air or water heat exchangers to about 32°C. The synthesis gas is now at a low enough temperature to be processed in the purification section.

Gas Purification

Depending upon the sulfur content of the coal fed to the gasifier, a certain amount of H_2S and other sulfur compounds will be present in the synthesis gas. These compounds must be removed to acceptable levels prior to the fuels end use. The CO_2 present may also be removed, depending upon the specific situation.

The purification step usually consists of a Rectisol unit to remove sulfur compounds and CO_2, if desired, from the synthesis gas stream. It is usually followed by a Claus or Stretford unit to recover the sulfur compounds as elemental sulfur.

Methanation

The methanation step is designed to convert the medium-Btu synthesis gas from the gas purification section to a high-Btu gas by Equations 3-5 and 3-8:

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O + Heat \qquad (3\text{-}5)$$

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O + Heat \qquad (3\text{-}8)$$

If ethylene is present it is hydrogenated to ethane and then the ethane is hydrocracked to methane according to Equations 3-9 and 3-10:

$$C_2H_4 + H_2 \rightleftarrows C_2H_6 \qquad (3\text{-}9)$$

$$C_2H_6 + H_2 \rightleftarrows 2CH_4 \qquad (3\text{-}10)$$

All of these reactions are promoted by a nickel catalyst designed specifically for methanation. In this stage the methane content of the gas is increased from around 15 percent to about 93 percent and, correspondingly, the heating value from around 3800 kcal/Nm^3 (430 Btu/scf) to 8400 kcal/Nm^3 (950 Btu/scf) (US-112).

Gas Compression and Dehydration

Following methanation the synthesis gas is compressed to a predetermined pressure. Then it is cooled in air and/or water heat exchangers and dehydrated. Dehydration is usually accomplished by one of the many common wet or dry systems. A typical unit may be a glycol dehydration system which uses triethylene glycol (TEG) as the drying agent.

Auxiliary Systems for Gasification Plant

In addition to the gas cleaning equipment just described, other facilities including a primary water treatment unit, an ammonia still, coal and by-product storage facilities, process steam and power generation facilities, and an oxygen plant are required for unit operations.

3.2.1.1 Module Basis

The high-Btu coal gasification module is based upon a facility capable of producing 7.1 x 10^6 Nm^3/day (250 x 10^6 scfd) of SNG with a heating value of 8,746 kcal/Nm^3 (983 Btu/scf). This size was selected since it corresponds to the capacity of the proposed WESCO Lurgi coal gasification complex to be constructed in the four-corners area of New Mexico. It is considered to be typical of the commercial plants to be constructed. Extensive information is available on this process, including heat and material balances and emission estimates. To produce 7.1 x 10^6 Nm^3/day of SNG the plant will process about 22,560 metric tons/day (24,820 TPD) of coal. A summary of emissions from the gasification plant is presented in Table 3.2-2. Emissions of trace elements and trace organics is discussed in Section 3.2.3.

TABLE 3.2-2. SUMMARY OF ENVIRONMENTAL IMPACT FROM LURGI HIGH-BTU COAL GASIFICATION

Basis: 7.1 x 10^6 Nm^3/day of Synthetic Natural Gas	
Air (kg/day)	
SO_2	10,970
NO_x	17,930
HC	210
NH	45
Particulate	790
Water (kg/day)	0
Thermal (kcal/hr)	Neg.
Solid Waste (MT/day)	5,940
Water Requirements (ℓ/min)	20,100
Energy Recovery Ratio	0.69
Manpower Requirements (personnel)	600
Ancillary Energy (kcal/day)	1.44 x 10^9

3.2.1.2 Module Description

The Lurgi high-Btu processing module consists of the gasifier, gas cleanup units, sections for upgrading the gas heating content, related auxiliary systems, steam production, and by-product recovery and storage. The coal feedstock for the module is a subbituminous coal with an analysis as shown in Table 3.2-3. The composition of the product gas is shown in Table 3.2-4.

TABLE 3.2-3. GASIFICATION COAL ANALYSES

Component	Wt %
Ash	22.79
H_2O	12.00
Sulfur	0.74

Heating Value = 4622 kcal/kg (8325 Btu/lb)
Source: US-349

TABLE 3.2-4. COMPOSITION OF THE SNG PRODUCT FROM DESIGN BASIS LURGI PLANT

Component	Vol. %
CH_4	96.84
CO_2	0.50
CO	0.06
H_2	1.45
N_2 + Air	1.15
Total	100.00

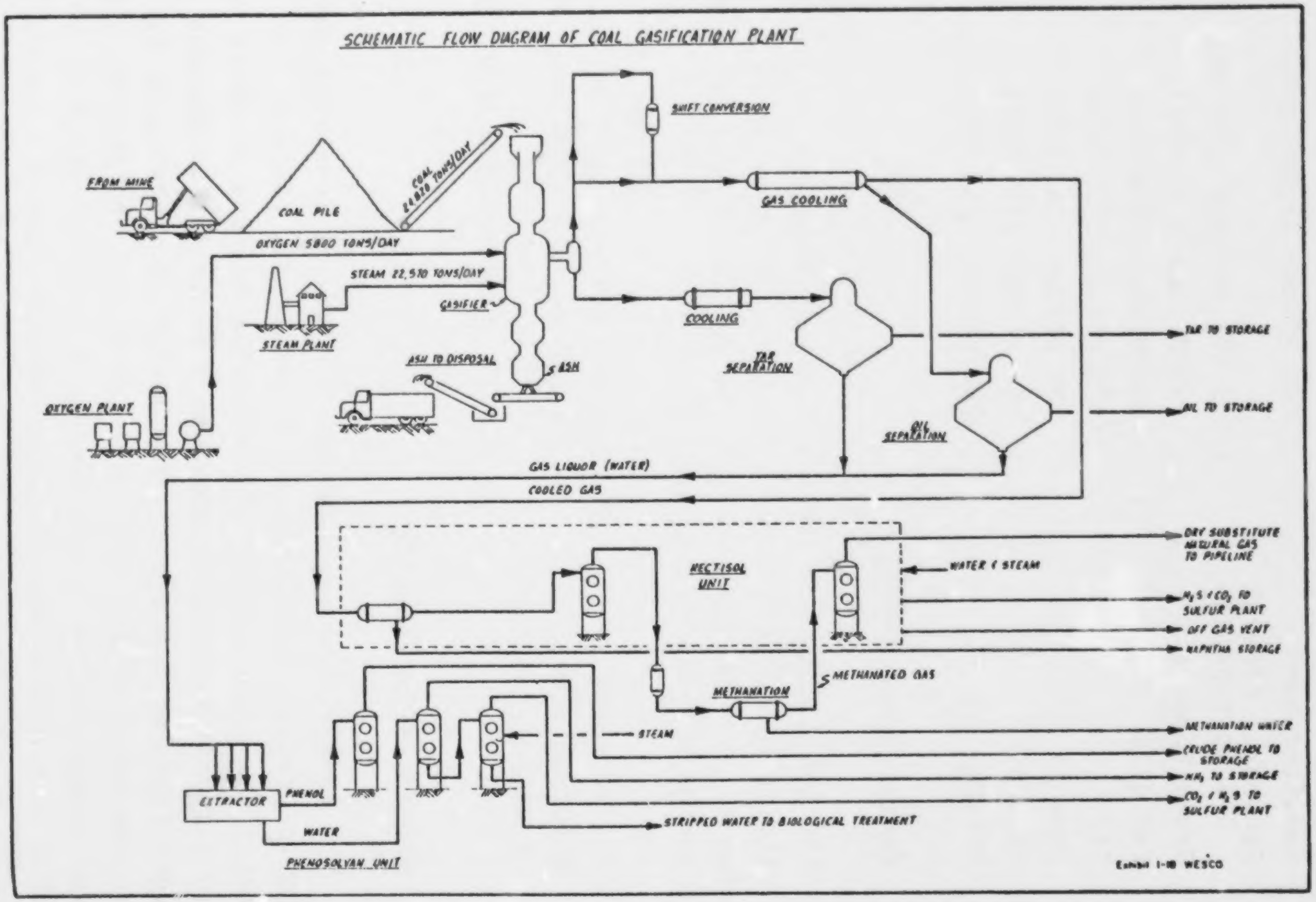
Heating Value = 8746 kcal/Nm (983 Btu/scf)
Source: US-349

Processing Steps

The basic processing steps of the Lurgi coal gasification process are shown in Figure 3.2-3. Sized coal is reacted with steam and oxygen in the gas production area, producing a raw synthesis gas. This gas then undergoes 1) shift conversion to produce the proper H_2:CO ratio for the methanation reactor, 2) cooling, 3) purification, 4) methanation and 5) dehydration and compression. The auxiliary or by-product recovery areas provide the facilities with water treatment, auxiliary power generation, process heat dissipation and by-product recovery and storage.

Flow Rates

The module flow rates have been taken from the Final EIS on the WESCO coal gasification plant. The rates for the major process streams are:



Source: US-349

FIGURE 3.2-3 OVERALL LURGI FLOW DIAGRAM

Coal to Gasifier - 22,560 MT/day (24,820 TPD)
Gasifier Ash - 5,940 MT/day (6,534 TPD)
Synthetic Natural Gas to Pipeline - 7.1 x 10^6 Nm^3/day (250 MMscfd)
Crude Phenols - 93 MT/day (102 TPD)
Tar Oils - 686 MT/day (755 TPD)
Tar - 675 MT/day (743 TPD)
Ammonia - 185 MT/day (204 TPD)
Naphtha - 286 MT/day (315 TPD)
Sulfur - 184 MT/day (202 TPD)

Energy Requirements

The Lurgi coal gasification process requires auxiliary energy in the form of electricity and steam. To provide this energy, coal is used to fire steam boilers. The energy requirements for the major plant users are:

Boiler Plant - 817.2 x 10^5 kcal/hr (3237 MMBtu/hr)
Electric Power - 60.1 x 10^5 kcal/hr (239 MMBtu/hr)
Steam Superheater Fuel Oil - 81.4 x 10^6 kcal/hr (323 MMBtu/hr)

Energy Recovery Ratio

The energy recovery ratio is a means of measuring the raw energy to product efficiency for a particular process. In the synthetic fuels processing industry this measure is an important consideration since it provides a basis for comparison of different types of processes. The energy recovery ratio is defined as the ratio of the heating value of all the primary products to the heating value of the feedstock and fuel input to the module. For this module the primary product is the SNG with a heating value of 8746 kcal/Nm^3. The average heating value of the feedstock is 4622 kcal/kg. The energy recovery ratio for the Lurgi high-Btu gasification module is 0.69 (US-349).

Water Requirements

The water requirements for this module are based upon the WESCO coal gasification plant. They estimate a water requirement of 20,100 liters/min (5309 gpm).

3.2.1.3 Module Emissions

This section contains multimedia emission estimates from the Final Environmental Statement for the WESCO Coal Gasification Project (US-349). Trace element and trace organic emissions are discussed separately in Section 3.2.3.

Air Emissions

Atmosphere emissions from the Lurgi facility result from process and fugitive emission sources.

Process Emissions

Process sources include the coal lock hopper, steam boiler, steam superheater, gas liquor expansion gas, gas liquor vent gas, shift catalyst regeneration, Rectisol vent gas, Claus sulfur plant, and Stretford plant. Table 3.2-5 contains the WESCO EIS emission estimates for the process sources (US-349).

Emissions from the coal lock occur during the decompression cycle and the loading of the lock with coal. The gas is vented to the atmosphere after particulate removal. The control efficiency of the particulate removal device is unknown.

TABLE 3.2-5. PROCESS ATMOSPHERIC EMISSIONS FROM HIGH-BTU LURGI COAL GASIFICATION

Source	Stack Diameter (m)	Stack Height (m)	No. of Stacks	Emissions for Total Stacks (kg/day)			
				SO_2	NO_x	HC	Particulates
Coal lock	2.73	60.61	1	744	1,056	10,824	24
Rectisol Vent gas				1,848	---	---	---
Steam boilers				5,832	15,816	---	744
Steam superheater				360	1,056	---	24
Claus sulfur plant	5.15	90.90	1	1,320	---	---	---
Strerford plant				168	---	---	---
Gas liquor expansion				336	---	---	---
Gas liquor vent gas				168	---	---	---
Recovered hydrocarbons				192	---	---	---
TOTAL				10,968	17,928	10,824	792

Particulate emissions from the steam boiler are controlled by electrostatic precipitators in combination with wet scrubbers (US-349). Typical control efficiencies for this combination is greater than 99 percent. After particulate removal, the flue gases are combined with those from the steam superheater and vented to the atmosphere via the large ninety meter (300 ft) stack. The vented vapors from the gas liquor expansion and gas liquor vent, shift catalyst regeneration, Rectisol unit, Claus sulfur plant, and Stretford plant are incinerated in the plant steam boiler and combined with the flue gases from the boiler and superheater and sent to the large stack. Incineration controls virtually 100 percent of the hydrocarbon and carbon monoxide emissions.

Figure 3.2-4 is a simplified diagram showing the disposition of the streams originating from the Rectisol Unit. The rich H_2S stream goes to the Claus sulfur plant. The lean H_2S stream is routed to the Stretford Plant. The CO_2 off-gas vent is sent to the plant boilers for incineration since it contains from 1 to 3 percent hydrocarbons. Incineration in the boilers should reduce the hydrocarbon emissions from this source by 100 percent.

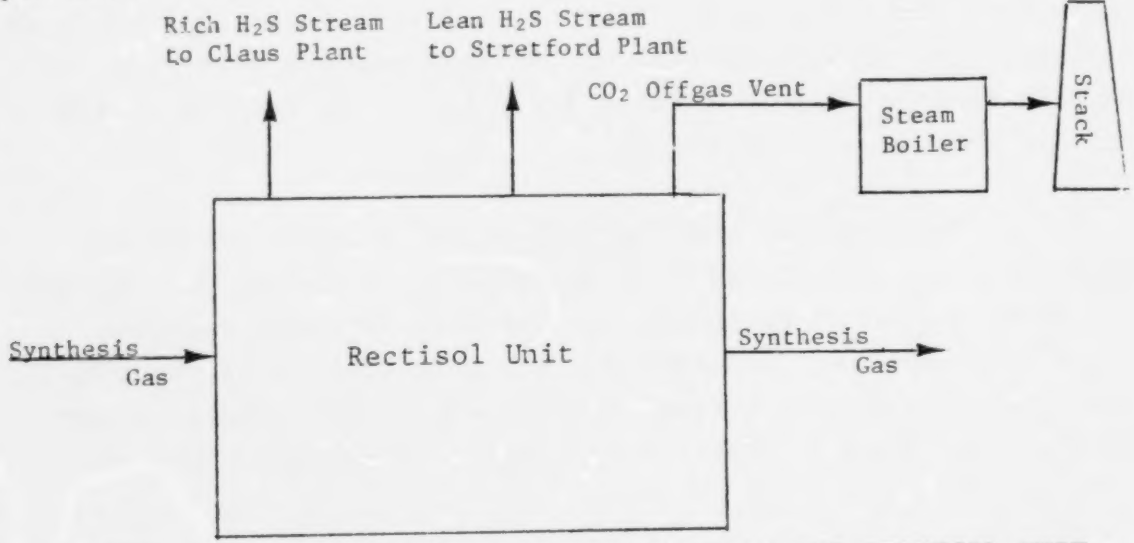


FIGURE 3.2-4 DISPOSITION OF STREAMS FROM THE RECTISOL UNIT

Intermittent emissions orginate from the local vent and the plant flare. These emissions occur during startup or emergency conditions. WESCO estimates emissions from the local vent to be 1.8 MT/yr of SO_2 and 1.0 MT/yr of hydrocarbons. From the flare, WESCO estimates 4.7 MT/yr of SO_2 are emitted.

Fugitive Atmospheric Emissions

Fugitive air emissions from the Lurgi gasification process arise from equipment leaks such as pump seals, valves, and flanges. Emissions from storage facilities are included. High pressures encountered in many of the processing operations of the Lurgi process enhance fugitive leaks from equipment. It is assumed that fugitive emission losses are minimized by use of the best available control techniques, including mechanical seals on pumps and vapor recovery systems on storage facilities. In addition, it is assumed that good maintenance practices are employed to help minimize equipment leaks.

By-product storage losses are calculated using the method outlined in API Bulletin No. 2523 (AM-030) and information in Compilation of Air Pollutant Emission Factors (EN-071). Vapor recovery systems with a 95% recovery efficiency are assumed to be employed for emission control on the by-product hydrocarbon and ammonia storage vessels. Table 3.2-6 lists the results of the storage emissions calculations.

Estimates of the fugitive emissions from valves and pump seals are calculated from an emission factor of 0.23 kg/day for these pieces of equipment when used in refinery services (DA-069). Pump seal emission factors were doubled if the pump handled high-pressure streams and halved if they handled water/hydrocarbon streams. Table 3.2-7 lists the adjusted pump seal emission factors, the number of pumps for each type of service, and the pump seal emissions. All pumps are assumed to use mechanical seals. Table 3.2-8 lists the valve emission factors, the estimated number of valves and the valve emissions.

TABLE 3.2-6. BY-PRODUCT STORAGE EMISSION LOSSES

	Naphtha	Tar Oil	Tar	Phenols	Ammonia
Total losses (kg/day)	769	745	493	90	1730*
Total losses employing vapor recovery (kg/day)	38.5	20.3	13.4	2.4	45.3*

*Emission rate based on vapors being 96% NH_3.

TABLE 3.2-7. PUMP SEAL EMISSIONS

Type of Stream Handled by Pump	Number of Pumps	Emission Factor, kg/day	Air Emission, kg/dav
Water/Hydrocarbon Stream (low pressure)	18	0.05	0.9
Hydrocarbon Stream (low pressure)	48	0.10	4.8
or	48	0.10	4.8
Water Hydrocarbon Stream (high pressure)			
Gaseous Stream (high pressure)	12	0.20	2.4
TOTAL			12.9

TABLE 3.2-8. FUGITIVE EMISSIONS FROM VALVES

Type of Service in Which Valve in Used	Number of Valves	Emission Factor, kg/day	Air Emission, kg/day
Gaseous	930	0.100	93
Liquid	1360	0.022	30
TOTAL			123

The composition of the fugitive emissions from valves and pump seals is a mixture of the various hydrocarbon streams found in the Lurgi plant. The discussion in Section 3.2.3 describes the compounds that may be present in the Lurgi process and are potential fugitive emissions.

Liquid Effluents

The Lurgi coal gasification process is designed to operate with "zero liquid discharge." All potential liquid effluents are either treated for reuse within the process or sent to evaporation ponds for disposal. Plant runoff is collected in a storm water pond and then treated in the normal wastewater treating system. Thus, no liquid effluents are discharged from the boundary limits of the conversion facility.

Solid Wastes

Solid wastes from the Lurgi coal gasification plant consist of 1) gasifier ash, and 2) lime softener sludge.

The coal fed to the gasifiers contains 22.79 weight percent ash. Since all of this ash is removed from the gasifiers and sent to ash quenching, approximately 247,500 kg/hr of ash is produced based on a coal rate to the gasifiers of 22,560 MT/day.

The gasifier ash contains a major portion of the trace elements present in the coal feedstock. In addition, trace organics could be present in the ash effluent. The existence and composition of these pollutants in the gasifier ash are discussed in Section 3.2.3.

Approximately 230 kg/hr of $CaCO_3$ is produced in the lime softener. These solids are transported in slurry form to the ash quenching area where they are combined and disposed of with the gasifier ash. The total solid waste to disposal is 247,700 kg/hr (511,400 lb/hr).

3.2.2 Low- and Medium-Btu Gasification

The gasification of coal by the Lurgi process to produce either a low- or medium-Btu gas is an alternative to high-Btu gasification. Low-Btu fuel gas has a heating value of 1330-2660 kcal/Nm^3 (150-300 Btu/scf) and can be used as fuel in either a conventional boiler or a combined cycle generating plant. Medium-Btu gas has a heating value of 2660-4000 kcal/Nm^3 (300-450 Btu/scf). It can be used as a chemical feedstock or as fuel in a conventional boiler or a combined cycle power generating plant.

Low- and medium-Btu Lurgi gasification differ only in the source of oxygen for the gasifier. The medium-Btu scheme requires a 98%+ oxygen stream to the gasifier supplied by a cryogenic oxygen plant while the low-Btu complex operates with an air-blown gasifier as its source of O_2. The nitrogen which enters the low-Btu gasifier in the air dilutes the synthesis gas, resulting in a lower heating value for the product.

Figure 3.2-5 shows a simplified flow diagram of low- and medium-Btu gasification. The primary difference between the high-Btu process and the low- and medium-Btu processes is the synthesis gas upgrading stages. Shift conversion and methanation reactors are not present in low- or medium-Btu plants. The remaining processes are discussed in Section 3.2.1.

3.2.2.1 Module Basis

The two modules are based on an output equivalent to the high-Btu module on a Btu/day basis. The output from the high-Btu module is 6.2 x 10^{10} kcal/day (2.45 x 10^{11} Btu/day) based on a product gas with a heating value of 8746 kcal/Nm^3 (983 Btu/scf). The heating value for the low-Btu product gas is 1785 kcal/Nm^3 (200 Btu/scf) and for the medium-Btu product gas is 4080 kcal/Nm^3 (450 Btu/scf). The product flow rates are adjusted to these numbers. Therefore, the low-Btu module produces 34.5 x 10^6 Nm^3/day (1.22 x 10^9 scfd) and the medium-Btu module produces 15.4 x 10^6 Nm^3/day (5.44 x 10^8 scfd).

Summaries of emissions for low- and high-Btu gasification plants are presented in Tables 3.2-9 and 3.2-10.

3.2.2.2 Module Descriptions

Separate descriptions are not provided since the low- and medium-Btu modules are similar to the high-Btu module described in Section 3.2.1.2.

3.2.2.3 Module Emissions

The emissions are calculated using the Wesco Final EIS. Emissions should be similar to the emissions discussed for high-Btu gasification in Section 3.2.1.3. However, more stringent

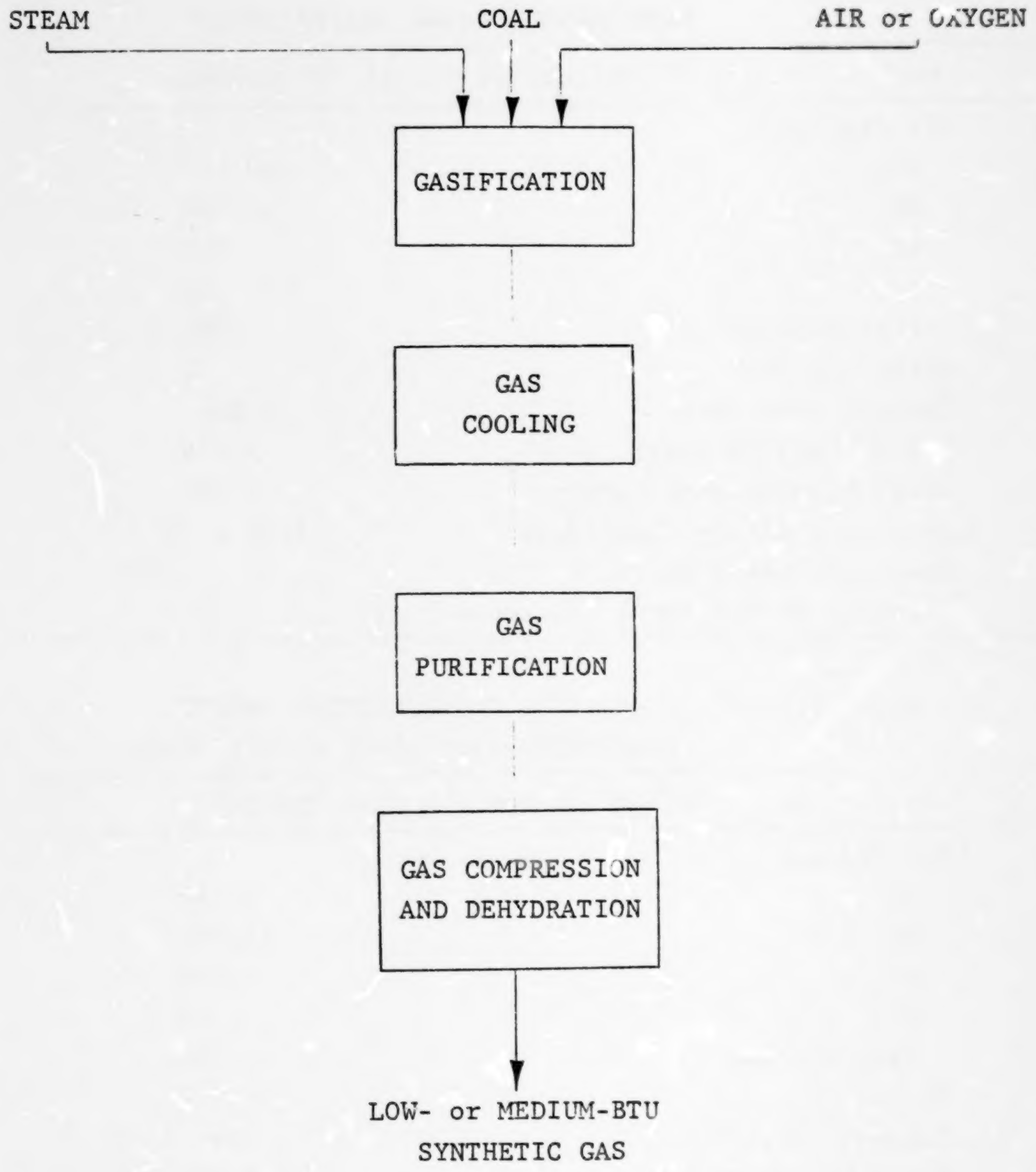

STEAM
COAL
AIR or OXYGEN
GASIFICATION
GAS COOLING
GAS PURIFICATION
GAS COMPRESSION AND DEHYDRATION
LOW- or MEDIUM-BTU SYNTHETIC GAS

FIGURE 3.2-5. GENERAL FLOW DIAGRAM OF LURGI LOW- OR MEDIUM-BTU GASIFICATION

TABLE 3.2-9. SUMMARY OF ENVIRONMENTAL IMPACT FROM LOW-BTU LURGI GASIFICATION

Basis: 34.5 x 10^6 Nm^3/day of gas (1,220 MMscfd)	
Air (kg/day)	
SO_2	10,100
NO_x	17,930
HC	210
NH_3	40
Particulates	792
Water (kg/day)	0
Thermal (kcal/hr)	Neg
Solid Waste (MT/day)	5,470
Water Requirements (ℓ/min)	18,400
Ancillary Energy (kcal/day)	1.67 x 10^9
Energy Recovery Ratio	.758
Manpower Requirements (personnel)	600

TABLE 3.2-10. SUMMARY OF ENVIRONMENTAL IMPACT FROM MEDIUM-BTU LURGI GASIFICATION

Basis: 15.4 x 10^6 Nm^3/day of gas (544 MMscfd)	
Air (kg/day)	
SO_2	9,740
NO_x	17,930
HC	210
NH_3	40
Particulates	792
Water	0
Thermal (kcal/hr)	Neg
Solid Waste (MT/day)	5,280
Water Requirements (ℓ/min)	17,900
Ancillary Energy (kcal/day)	1.62 x 10^9
Energy Recovery Ratio	.784
Manpower Requirements (personnel)	600

sulfur removal must be performed in the low-Btu Rectisol unit due to nitrogen dilution of the product gas. This accounts for differences in SO_2 emission rates.

3.2.3 Trace Element and Organic Emissions from Coal Gasification

Available data concerning the formation and fate of trace organics and elements in coal gasification processes is very limited. However, limited analogies can be drawn between the gasification process and the conventional coking and coal combustion processes to give insight into the identification, quantification, and ultimate fate of trace compounds produced in the gasification process. The following sections discuss these analogies and present some of the available literature data.

3.2.3.1 Trace Elements

Elements present in concentrations of 0.1% (1,000 ppm) or less are usually referred to as trace elements. The main source of the trace elements found in coal is the mineral matter associated with living plant tissues. Table 3.2-11 lists the trace element analysis of a typical western coal.

Little information is available on the fate of trace elements in a coal gasification plant. An analogy, however, can be drawn between coal gasification and coal combustion. Basically the same trace elements will be in the coals fed to both systems. Also, the gasification system includes a section in which the coal passes through an oxidizing atmosphere similar to that present in a boiler. However, this analogy has its limitations.

TABLE 3.2-11. TRACE ELEMENT CONCENTRATION IN TYPICAL WESTERN COAL

Element	ppm by weight
Antimony	0.3 - 1.2
Arsenic	0.1 - 3.0
Bismuth	0.0 - 0.2
Boron	60.0 - 150.0
Bromine	0.4 - 18.0
Cadmium	0.2 - 0.4
Fluorine	200.0 - 780.0
Gallium	0.5 - 8.0
Germanium	0.1 - 0.5
Lead	1.4 - 4.0
Mercury	0.2 - 0.3
Nickel	3.0 - 30.0
Selenium	0.1 - 0.2
Zinc	1.1 - 27.0

Source: US-112

As shown in Figure 3.2-6, coal fed into a power plant boiler encounters only an oxidizing atmosphere. Coal combustion products exist in either the gas or solid phase. In the gasifier, the coal first encounters a reducing atmosphere. Part of the coal is vaporized and leaves the system while the char which remains enters the combustion zone at the bottom of the gasifier. In this oxidizing atmosphere, the char is combusted with oxygen in the presence of steam. This produces a gas mixture containing hydrogen which is fed to the top section of the gasifier. Because trace elements in a Lurgi gasifier first encounter a reducing atmosphere, then an oxidizing atmosphere (with possible recycle through the reducing atmosphere), it is difficult to predict the distributions of specific trace elements among the Lurgi gasifier effluent streams.

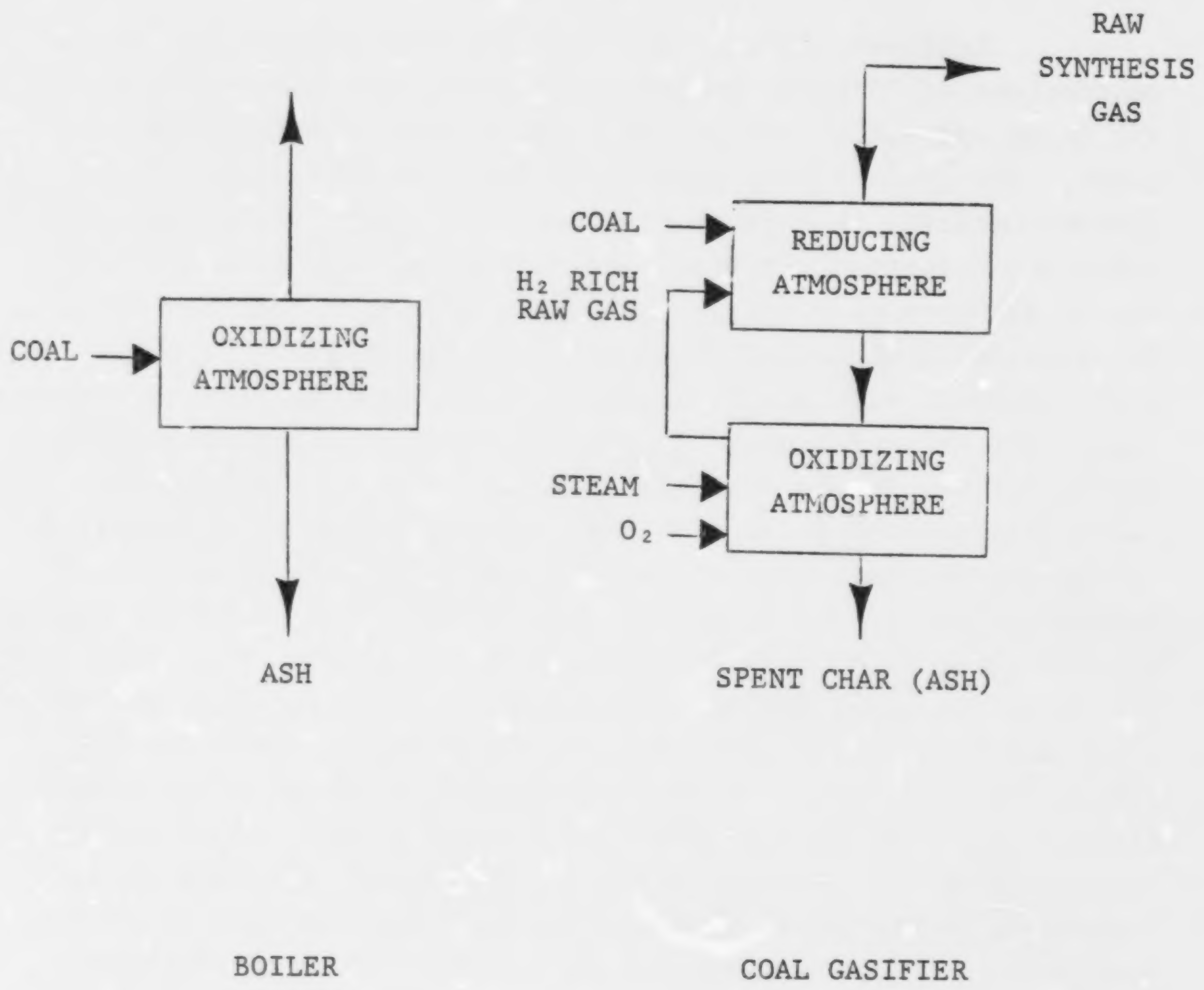


FIGURE 3.2-6. COMPARISON OF ENVIRONMENTS IN A BOILER AND A COAL GASIFIER

Experimental Studies of the Fate of Trace Elements in Coal Processing Systems

Kaakinen, Jorden, and West (KA-121) determined the concentrations of 17 trace elements and total mass flow rates for all inlet and outlet streams of a pulverized coal-fired power plant. The goal of this effort was the calculation of a trace element material balance around the power plant. Aluminum, iron, rubidium, strontium, yttrium, and niobium concentrations in all outlet ash streams (fly ash and bottom ash) were reported to be essentially unchanged from inlet concentrations. Copper, zinc, arsenic, molybdenum, antimony, lead, and the radioisotopes lead - 210 and polonium - 210 were found in progressively higher concentrations in fly ash fractions collected in a downstream direction from the firebox. These trace elements were in their lowest concentrations in the bottom ash. The bulk of the inlet concentrations of the trace elements found in both of these groups were retained in the solid samples. The inability to account for the inlet concentration of mercury and selenium in solid and liquid samples suggests that portions of these two elements existed as vapors and/or very fine aerosols in flue gas which passed through the sampling equipment. Also, the enrichment of certain trace elements in successive fly ash fractions collected in the downstream direction is probably due to volatilization of these elements or their compounds in the furnace and their subsequent condensation or adsorption onto suspended fly ash particles. Natusch, Wallace, and Evans (NA-149) likewise report that the trace elements arsenic, antimony, cadmium, lead, selenium, and thallium probably volatilize in the furnace and recondense on small ash particles as the flue gas cools.

A Radian report (RA-R-219) characterizes trace element emissions from three coal-fired electric generating stations. A material balance approach was used for a quantitative examination of twenty-seven elements. The results indicate that the trace elements can be classified into two general groups: 1) those preferentially emitted with the flue gas, and 2) those uniformly distributed in the ash. The elements included in this study include the following:

aluminum
antimony
chlorine
chromium
cobalt
copper
fluorine
arsenic
barium
iron
lead
magnesium
manganese
mercury
beryllium
boron
mercury
molybdenum
nickel
selenium
silver
cadmium
calcium
sulfur
titanium
uranium
vanadium
zinc

Enrichment in the flue gas at all three stations was indicated for:

sulfur
mercury
chlorine
antimony
fluorine
selenium
lead
molybdenum
nickel
boron
zinc
cadmium
chromium
copper
cobalt
uranium
arsenic
silver

The remainder of the twenty-seven elements were found to exit the stack in the same proportion as they exit with the ash. These were:

barium
beryllium
vanadium
aluminum
calcium
iron
manganese
magnesium
titanium

Another Radian study used the Radian Equilibrium Program to predict the fate of trace elements in a Lurgi gasifier.

The program is described in Section 2.2.4.1. and in the Appendix. The following trace elements were selected for consideration on the basis of both their presence in typical coals and interest as potential pollutants: As, Be, Se, Cd, Hg, Pb, B, Co, Cr, Cu, Ge, Mn, Mo, Ni, P, Sb, Sn, V, Zn, Ba, U. Table 3.2-12 presents the results of the study.

TABLE 3.2-12. FATE OF SELECTED TRACE ELEMENTS IN LURGI GASIFIER

Element	wt. ppm in Feed Coal	600°K	866°K
As	14.0	V	V
Be	1.6	NV	NV
Se	2.1	V	V
Cd	2.5	NV	V
Hg	0.2	V	V
Pb	35.0	V	V
B	102.0	V	V
Co	9.6	NV	NV
Cr	13.8	NV	NV
Cu	15.0	NV	NV
Ge	6.9	NV	V
Mn	49.0	NV	NV
Mo	7.5	NV	NV
Ni	21.0	NV	NV
P	71.0	V	V
Sb	1.3	V	V
Sn	4.8	NV	NV
V	33.0	NV	NV
Zn	272.0	NV	NV
Ba	130.0	NV	NV
U	1.3	NV	NV

V - Volatile
NV - Non volatile

Attari (AT-042) has reported data on coal gasification systems in connection with the IGT HYGAS pilot plant. The purpose of this work was to measure the concentration of eleven trace elements found in the solid streams entering and leaving each of the three stages of the HYGAS pilot plant. The HYGAS gasifier section is shown in Figure 3.2-7.

Because the pilot plant was not operational during the period when the analytical work was performed, coal and char samples accumulated over several years of bench-scale research were used in the analysis. The emphasis of the project was placed on trace element analytical methods since sampling and operating criteria of the pilot plant were not involved. The relative amounts of the trace elements found in the overhead gas and the spent char from the electrothermal gasifier are presented in Table 3.2-13. The amount of each element in the overhead gas was assumed to be the remainder unaccounted for in the spent char. It can be seen from these data that most of the Hg, Se, As, Te, Pb and Cd which entered the gasifier in the coal feed, apparently left the gasifier in the vapor phase. Most of the Sb, V, Nu, Be and Cr remained in the solid phase.

Some research has indicated that trace elements might also be found in the aqueous streams of a coal gasification system. Shown in Table 3.2-14 are Bureau of Mines data on trace elements which were detected in condensate from a laboratory Synthane gasifier.

The Northern Great Plains Resources Program Atmospheric Aspects Work Group published a report in 1974 which contains an estimation of the trace element emissions for a 7.1 x 10^6 Nm^3/day (250 MM scfd) gasification plant whose feedstock was an Eastern coal (NO-098). Table 3.2-15 presents the results. These estimates originate from an EIS done in 1973 by Rhodes for coal gasification.

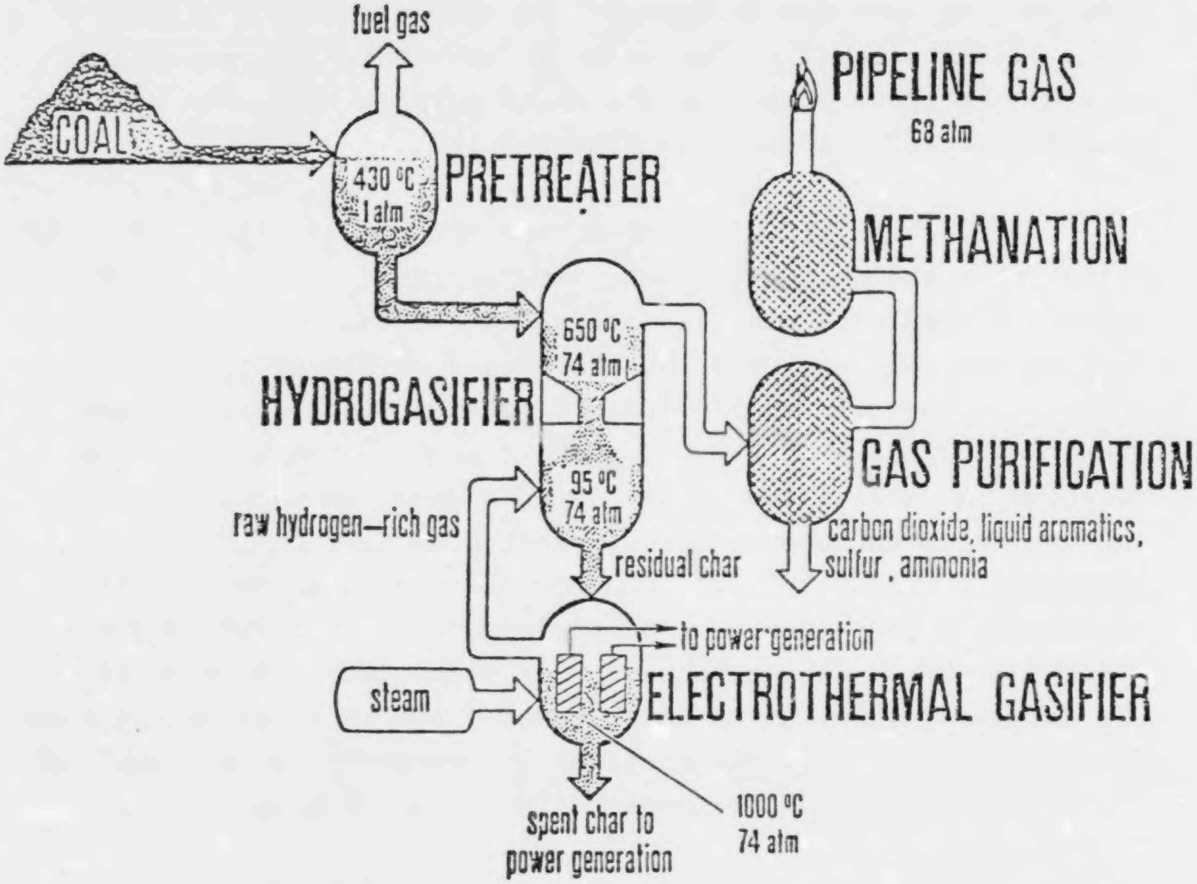


FIGURE 3.2-7. IGT HYGAS PROCESS FOR ELECTROTHERMAL GASIFICATION, SHOWING PRETREATMENT, HYDROGASIFICATION, AND ELECTROTHERMAL STAGES

TABLE 3.2-13. TRACE ELEMENT CONCENTRATION OF CHAR CALCULATED ON RAW COAL BASIS

Trace Element	Gas* Overhead (%)	Spent Char Bottom (%)
Hg	96	4
Se	74	26
As	65	35
Te	64	36
Pb	63	37
Cd	62	38
Sb	33	67
V	30	70
Ni	24	76
Be	18	82
Cr	0	100

*The % of the trace element in the overhead gas was calculated by the difference since only a solid analysis was done.

Source: AT-042

TABLE 3.2-14. TRACE ELEMENTS IN CONDENSATE FROM AN ILLINOIS NO. 6 GASIFICATION TEST

	No. 1	No. 2	Average (by weight)
Ppm:			
Calcium	4.4	3.6	4
Iron	2.6	2.9	3
Magnesium	1.5	1.8	2
Aluminum	0.8	0.7	0.8
Ppb:			
Selenium	401	323	360
Potassium	117	204	160
Barium	109	155	130
Phosphorus	82	92	90
Zinc	44	83	60
Manganese	36	38	40
Germanium	32	61	40
Arsenic	44	28	30
Nickel	23	34	30
Strontium	33	24	30
Tin	25	26	20
Copper	16	20	20
Columbim	7	5	6
Chromium	4	8	6
Vanadium	4	2	3
Cobalt	1	2	2

Source: FO-026

TABLE 3.2-15. TRACE ELEMENT EMISSIONS FROM A COAL GASIFICATION PLANT

Basis: 7.1 x 10^6 Nm^3/day

Element	Emissions (kg/day)
Arsenic	0.14
Bromine	0.15
Cadmium	0.01
Chromium	0.17
Cobalt	0.06
Copper	0.15
Flourine	1.01
Gallium	0.04
Lead	0.10
Manganese	0.54
Mercury	0.002
Nickel	0.15
Selenium	0.02
Vanadium	0.25

The above data clearly indicate the loss of certain trace elements during gasification. However, no conclusion as to the final disposition of all of the trace elements leaving the gasifier is possible. Also, the chemical forms in which the trace elements occurred were not examined in any of the streams.

Data Analysis

Based on the recent studies of trace elements in a coal-fired power plant (KA-121) and in a coal gasification system (AT-042), only limited conclusions can be made about the ultimate fate of trace elements in a Lurgi gasification plant. The HYGAS data cannot necessarily be related to the Lurgi gasification system. Furthermore, the samples analyzed (solids only) were from bench-scale work, and, therefore, may not be representative of commercial scale operation. Nevertheless, it is obvious from these studies that certain trace elements have a tendency to volatilize while others have a tendency to remain in the ash or spent char.

Data on the volatility of trace elements in coal as reported by Ruch, Gluskoter, and Shimp (RU-039) are given in Table 3.2-16. Results of the low-temperature (150°C) ash testing show that only Hg (up to 90 percent), Br (100 percent), and Sb (up to 50 percent) are volatilized. F was not tested but was assumed to be volatilized completely. Results of the high temperature (300 to 700°C) ash testing show that only Mo (33 percent) and V (up to 25 percent) are volatilized.

TABLE 3.2-16. VOLATILITY OF TRACE ELEMENTS IN COAL

Low-temperature ash			High-temperature ash		
Retained (> 95%)		Lost	Retained*		Lost
Ga	Cu	Hg (up to 90%)	Zn	Cd	Mo (33%)
Se	Pb	Br (100%)	Ni	Mn	V (possibly up to 25%)
As	V	Sb (up to 50%)	Co	Cr	
Zn	Mn	F (untested but presumed lost)	Cu	Be	
Ni	Cr		Pb	Ge	
Co	Cd		B	Sn	
Be				Se (untested but presumed retained)	

* No significant losses observed in coal ash from 300 to 700°C or between results from whole coal and low-temperature ash or high-temperature ash (∿450°C).

Source: RU-039

Analysis using the Radian Equilibrium Program predicted that the following trace elements would volatilize in a Lurgi gasifier:

As, Se, Hg, P, Sb, Pb, B

The following elements were predicted to not volatilize, thus leaving the gasifier in the char and ash:

Be, Co, Cr, Cu, Mn, Mo, Ni, Sn, V, Zn, Ba, U

The program also predicted that Cd and Ge would be nonvolatile at a gasifier temperature of 600°K but would volatilize at 866°K.

There seems to be some agreement in the studies that portions of the Hg and Se exist as vapors and/or fine aerosols in the gas stream. The gasification data also indicates that As, Te, Pb, and Cd volatilize to some degree and that a portion of these trace elements will leave the gasifier in the overhead gas stream (see Table 3.2-13). The power plant study concludes that Ce, Zn, As, Pb, Mo, and Sb will be at least partially volatilized in a furnace and then condensed or adsorbed onto suspended fly ash particles.

Trace elements reported to remain in the spent char in a gasifier were Sb, V, Ni, Be, and Cr (see Table 3.2-13). In the power plant study, Al, Fe, Rb, Sr, Y, and Nb concentrations were reported to be constant in all outlet ash streams. This implies that they were not volatilized during combustion.

The Northern Great Plains report stresses the preliminary nature of the estimates shown in Table 3.2-15. They are based upon a limited amount of data. NGP claims that actual emissions may vary by an order of magnitude or more.

3.2.3.2 Trace Organics

There are two major sources of organic materials from coal processing: those originally present in the coal which are released through volatilization and those formed by chemical reaction in the gasifier and associated equipment. Much information is known about the identity of individual components in coals. A significant amount of work has also been performed to define the products from coal pyrolysis or thermolysis. However, each coal has an individual genesis and a correspondingly unique composition. As a result the available data cannot be generalized and applied for all cases. It must be evaluated in terms of the coal composition and the process (reaction and operating conditions) involved.

Although the molecular composition pattern in coal cannot be specified precisely, a number of organic functional groups are present. A similar functional group pattern is probably present in the plant effluents. In processes which gasify coal at intermediate temperatures, the gasifier output may also contain all of the products commonly associated with pyrolysis, carbonization, and coking of coals in addition to the oxygenated products associated with partial combustion. It is unlikely that gasification conditions will result in complete conversion of all organic components to gas. The possibility exists, therefore, that traces of many organic compounds (functional groups) will be found in the plant effluent streams (RA-144).

Experimental Studies of the Fate of Trace Organics in Coal Processing Systems

Due to the lack of information concerning compositions of streams from a gasification plant, data on emissions from processes such as boilers and coke ovens, which have been characterized in more detail, were examined

Battelle (BA-261) reports forty-two toxic and hazardous organic substances likely to be emitted by industrial boilers (see Table 3.2-17). The organic compounds are listed in order of their decreasing health hazard. The first twelve compounds are all potent carcinogens. This rating is intended only as a guide since a direct comparison of the potency of the various hazardous materials is not always possible.

In the coke plant, cyclic and polycyclic organic matter present in coke oven emissions will be found primarily in the particulate fraction which has been defined as tar. The principal compounds obtained from coal tar as presented by (RO-153) and (MO-125) are given in Tables 3.2-18 and 3.2-19, respectively. Several of the more widely accepted carcinogens are species of benzpyrene. To characterize the presence of this general group, benzpyrene analyses were performed on the coal tar from a number of coke oven samples (BE-236). Results indicate that benzpyrene is present in concentrations ranging from less than 260 ppm to 18,000 ppm (Table 3.2-20). The combination of mass spectra and chromatographic data resulting from the above samples clearly indicates the presence of benz(c)phenanthrene (potent carcinogen), benz(a)anthracene (carcinogen), a benzfluoranthene isomer (possible carcinogen), benz(a)pyrene (potent carcinogen) and/or benz(e)pyrene, and cholanthrene (carcinogen).

As stated previously, the coal gasifier output may contain all of the products commonly associated with pyrolysis, carbonization, and coking of coals in addition to the oxygenated products associated with partial combustion. Various heavier organic compounds present may be classified as tar, including

TABLE 3.2-17. TOXIC AND HAZARDOUS SUBSTANCES LIKELY TO BE EMITTED BY INDUSTRIAL BOILERS

Organic Materials

7,12-Dimethylbenz(a)anthracene
3-methylcholanthrene
Dibenz(a,h)anthracene
Benz(c)phenanthrene

Benz(a)pyrene
Dibenz(a,h)pyrene
Dibenz(a,i)pyrene
Dibenz(c,g)carbazole

4-Aminobiphenyl
Benzidine
1-Naphthylamine
4-Nitrobiphenyl
Phenylhydrazine

Methyl-phenylhydrazine
Dibenz(a,j)acridine
Dibenz(a,h)acridine
Cholanthrene

Benz(j)fluoranthene
Benz(b)fluoranthene
Dibenz(a)anthracene
Dibenz(a,c)anthracene

Dibenz(a,j)anthracene
Dibenz(a,g)fluorene
Indeno(1,2,3-cd)pyrene
Dibenzo(a,l)pyrene

Benz(a)anthracene
Chrysene
Dibenz(a,c)fluorene
Dibenz(a,h)fluorene

Dibenz(a,i)carbazole
Benz(a)carbazole
Dibenz(c,h)acridine
Picene
Dibenz(a,g)carbazole

Benzoquinoline
Pyridine
Acridine
Aniline

Phenol
Benzthiophenes
Dibenzthiophenes
Thiophene

Source: BA-261

phenols and cresols, pyridines, anilenes, dihydric phenols (catechols), intermediate and high-boiling aromatics (naphthalenes), saturates, olefins, and thiophenes. Another group of organic compounds might be designated light oil and/or naphtha, including benzene-toluene-xylene (B-T-X), naphthalene, thiophene and condensable light hydrocarbons and carbon disulfide.

TABLE 3.2-18. PRINCIPAL COMPOUNDS OBTAINED FROM COAL TAR

Hydrocarbons	Nitrogen Compounds	Oxygen Compounds
Naphthalenes	Pyridines	Phenols
Acenaphthene	Quinoline	Cresols
Fluorene	Carbazole	Xylenol
Anthracene	Acridine	Naphthols
Phananthrene	Picoline	
Chrysene		
Pyrene		
Fluoranthene		

Source: RO-153

TABLE 3.2-19. COMPOUNDS OBTAINED FROM COAL TAR

Benzene	Phenanthrene
Toluene	Thiophrene
Xylenes	Thiophene
Phenols	Pyrole
Cresols	Pyridine
Naphthalenes	Quinoline
Anthracene	

Source: MO-125

TABLE 3.2-20. BENZPYRENE ANALYSIS COAL TAR FROM COKE OVEN

Test Number	Location	Sample Number	Total Benzpyrene (µg)	Benzpyrene Concentration* (ppm)
7	1	1045	30	510
8	2	1060	70	1,000
8A	3	1066	100	560
8A	3	1067	B.D.L.	<260
9	1	1095	B.D.L.	<630
10	6	1102	30	560
10	4	1105	B.D.L.	<1,300
11	4	1111	B.D.L.	<1,000
11	5	1114	B.D.L.	<590
19	1	1208	B.D.L.	980
20	2	1213	B.D.L.	<1,400
21	3	1222	22,000	18,000
21	3	1223	520	3,000
21	3	1229	B.D.L.	<610
23	2	1241	220	1,700

* µg of Benzpyrene/gram of Tar

Source: BE-236

In a study of the effluent from an experimental coal gasification plant, certain organic components were extracted and tentatively identified (Table 3.2-21). The particular distribution of organic compounds which might be present in raw gasifier gas will depend on the composition of the feed coal and on the operating conditions of the gasifier. The range of sulfur and B-T-X components which might be expected from the Synthane Process, another gasification process, are given in Table 3.2-22 for six coal feeds (FO-026, KA-142).

TABLE 3.2-21. COMPOUNDS TENTATIVELY IDENTIFIED IN WASTE EFFLUENT OF COAL GASIFICATION PILOT PLANT

Restructured Gas Chromatograph Peak	Best Match	Second Best Match
1	Phenol	Phenol
2	o-Cresol	m-Cresol
3	m-Cresol	o-Cresol
4	2,5-Dimethylphenol	2,6-Dimethylphenol
5	3,4-Dimethylphenol	3,4-Dimethylphenol
6	2.4-Dimethylphenol	3,4-Dimethylphenol
7	α-Naphthol	1,2-Dihydroxy-1,2-Dihydronaphthalene

Source: MC-130

Separation equipment is provided in the Lurgi gasification plant to remove condensable matter. Tars which might separate from such condensate have been partially characterized for the Synthane Process (Table 3.3-23). Similarly, aqueous condensate from Synthane raw gas has been analyzed and compared with coke-plant weak ammonia liquor (Table 3.3-24). These analyses of Synthane streams should qualitatively parallel the Lurgi gasifier streams since both operate at approximately the same temperature.

TABLE 3.2-22. COMPONENTS IN SYNTHANE GASIFIER GAS, ppm

	Illinois No. 6 Coal	Illinois Char	Wyoming Subbi-tuminous Coal	Western Kentucky Coal	North Dakota Lignite	Pitts-burgh Seam Coal
H_2S	9,800	186	2,480	2,530	1,750	860
COS	150	2	32	119	65	11
Thiophene	31	.4	10	5	13	42
Methyl thiophene	10	.4	--	--	--	7
Dimethyl thiophene	10	.5	--	--	11	6
Benzene	340	10	434	100	1,727	1,050
Toluene	94	3	59	22	167	185
C_8 aromatics	24	2	27	4	73	27
SO_2	10	1	6	2	10	10
CS_2	10	--	--	--	--	--
Methyl mercaptan	60	.1	.4	33	10	8

Source: FO-026,.KA-142

TABLE 3.2-23. MASS SPECTROMETRIC ANALYSES OF THE BENZENE-SOLUBLE TAR FROM THE SYNTHANE PROCESS (UNITS: VOLUME PERCENT)

Structural type (includes alkyl derivatives)	Run HP-1 No. 92, Illinois[1] No. 6 coal	Run HPL No. 94, lignite	Run HPM No. 111, Montana subbituminous coal	Run HP-118 No. 118,[1] Pittsburgh seam coal
Benzenes	2.1	4.1	3.9	1.9
Indenes	[2]8.6	1.5	2.6	[2]6.1
Indanes	1.9	3.5	4.9	2.1
Naphthalenes	11.6	19.0	15.3	16.5
Fluorenes	9.6	7.2	9.7	10.7
Acenaphthenes	13.5	12.0	11.1	15.8
3-ring aromatics	13.8	10.5	9.0	14.8
Phenylnaphthalenes	9.8	3.5	6.4	7.6
4-ring pericondensed	7.2	3.5	4.9	7.6
4-ring catacondensed	4.0	1.4	3.0	4.1
Phenols	2.8	13.7	5.5	3.0
Naphthols	([2])	9.7	9.6	([2])
Indanols	.9	1.7	1.5	.7
Acenaphthenols	--	2.5	4.6	2.0
Phenanthrols	2.7	--	.9	--
Dibenzofurans	6.3	5.2	5.6	4.7
Dibenzothiophenes	3.5	1.0	1.5	2.4
Benzonaphthothiophenes	1.7	--	--	--
N-heterocyclics[3]	(10.8)	(3.8)	(5.3)	(8.8)
Average molecular weight	212	173	230	202

[1] Spectra indicate traces of 5-ring aromatics.

[2] Includes any naphthol present (not resolved in these spectra).

[3] Data on N-free basis since isotope corrections were estimated.

Source: FO-026, KA-142

TABLE 3.2-24. BYPRODUCT WATER ANALYSIS FROM SYNTHANE GASIFICATION OF VARIOUS COALS [mg/ℓ (Except pH)]

	Coke plant	Illinois No. 6 coal	Wyoming subbituminous coal	Illinois char	North Dakota lignite	Western Kentucky coal	Pittsburgh seam coal
pH	9	8.6	8.7	7.9	9.2	8.9	9.3
Suspended Solids	50	600	140	24	64	55	23
Phenol	2,000	2,600	6,000	200	6,600	3,700	1,700
COD	7,000	15,000	43,000	1,700	38,000	19,000	19,000
Thiocyanate	1,000	152	23	21	22	200	188
Cyanide	100	0.6	0.23	0.1	0.1	0.5	0.6
NH_3	5,000	[1]8,100	9,520	2,500	7,200	10,000	11,000
Chloride	--	500	--	31	--	--	--
Carbonate	--	[2]6,000	--	--	--	--	--
Bicarbonate	--	[2]11,000	--	--	--	--	--
Total sulfur	--	[3]1,400	--	--	--	--	--

[1] 85 percent free NH_3

[2] Not from same analysis.

[3] $S^=$ = 400
$SO_3^=$ = 300
$SO_4^=$ = 1,400
S_2O_3 = 1,000

Source: FO-026, KA-142

Data Analysis

Due to the lack of available information, the best conclusions as to the ultimate fate of trace organics in a coal gasification plant must be estimates based on the composition of the coal, processing conditions, and data on actual emissions from a few processes such as boilers or coke ovens which have been characterized in more detail.

The direct bearing of the initial coal composition on possible effluents from a gasification plant is difficult to assess. However, it is expected that the coal function groups will be maintained to a certain extent. The following types of potential polluting compounds may be present in the Lurgi plant effluents to a greater or lesser degree. The listing is intended to be illustrative, not comprehensive (AN-062, BL-040).

Hydrocarbons
- Benzene
- Toluene
- Xylenes
- Polycyclic Aromatics
  - Naphthalenes
  - Anthracenes
  - Pyrenes

Oxygen-Containing
- Aromatic Acids
- Phenols
- Fatty Acids
- Esters
- Ethers
- Quinones
- Cresols
- Heterocycles (esters, lactones)

Sulfur-Containing
- Thiols
- Heterocycles

Nitrogen-Containing
- Heterocycles (pyridines, pyrroles, indoles, quinolines, carbazoles)

As previously stated, certain analogies can be drawn between coal combustion and coal gasification processes. However, conclusions drawn from an industrial boiler study should be applied to gasification plants only when the conditions of combustion are the same. Research on hazardous emissions from industrial boilers (BA-261) indicates that carcinogenic trace hydrocarbons are likely to be emitted. It is not possible to estimate the concentration of each of the components in the stack gas since only benz(a)pyrene has been studied in any detail (HA-011).

Analogies can also be made between coke ovens and coal gasifiers. Comparison of Tables 3.2-18, 3.2-19, and 3.2-23 reveals that several classes of organic compounds are present in the tar from both a coke oven and a gasifier. Coke ovens also operate in the same temperature range as some gasification processes, although at a much lower pressure. The results of the study of coke oven emissions indicate the presence of organic compounds widely accepted as carcinogens in relatively heavy concentrations in the tar. It is likely that some of these hazardous hydrocarbons are also present in gasifier tar.

Sampling and analyses of bench-scale Synthane gasifier effluents indicate trace organics present in the gasifier gas, the tar, and the by-product water streams. However, even these effluent streams are reported to be only representative of those that will be obtained from a commercial operation. The applicability of this data to a commercial operation has not been proven.

Based on solubility data, certain groups of trace organics will be expected to be almost totally in the organic process streams while others might be in the aqueous streams as well. Indenes, indanes, naphthalenes, fluorenes, acenaphthenes, and naphthols and dibenzofurans are insoluble in water and should remain almost totally within the organic streams. Benzenes, N-heterocyclics, phenols, and catechols are soluble in water and might, therefore, be in both aqueous and organic streams. Organics that are in the aqueous stream even in trace amounts could be concentrated and emitted from the Lurgi cooling water system.

4.0 PROCESS WATER SYSTEMS

This section of the report presents a detailed discussion of the water systems for the TOSCO II oil shale retorting process and the Lurgi coal gasification process. The discussion centers on the water system requirements and potential problem areas that can arise as these processes attempt to operate with zero discharge of water effluents.

The major water streams of interest are characterized according to flowrate and approximate compositions. Based on this information, individual system processes will be analyzed to evaluate problem areas. Examples of process problems include $CaCO_3$ and $CaSO_4$ scaling, and NH_3 and H_2S odor problems.

4.1 TOSCO II Process Water System

The Colony Development Operation plans to construct an underground oil shale mine and a TOSCO II oil shale plant consisting of retorting and upgrading facilities. The plant site will be located north of Grand Valley, Colorado, on Colony's Dow West oil shale field. The water system for the plant is discussed in this section.

Figure 4.1-1 is a schematic of the major process water streams. Because the Colony water system is designed to operate at zero discharge, all of the process water is eventually evaporated or consumed in moisturizing processed shale for disposal.

The plant water systems cascade the water streams from one process step to the next. In this manner, the best quality water is used in the process steps in which it is required. Blowdown streams from these processes are sent to processing steps

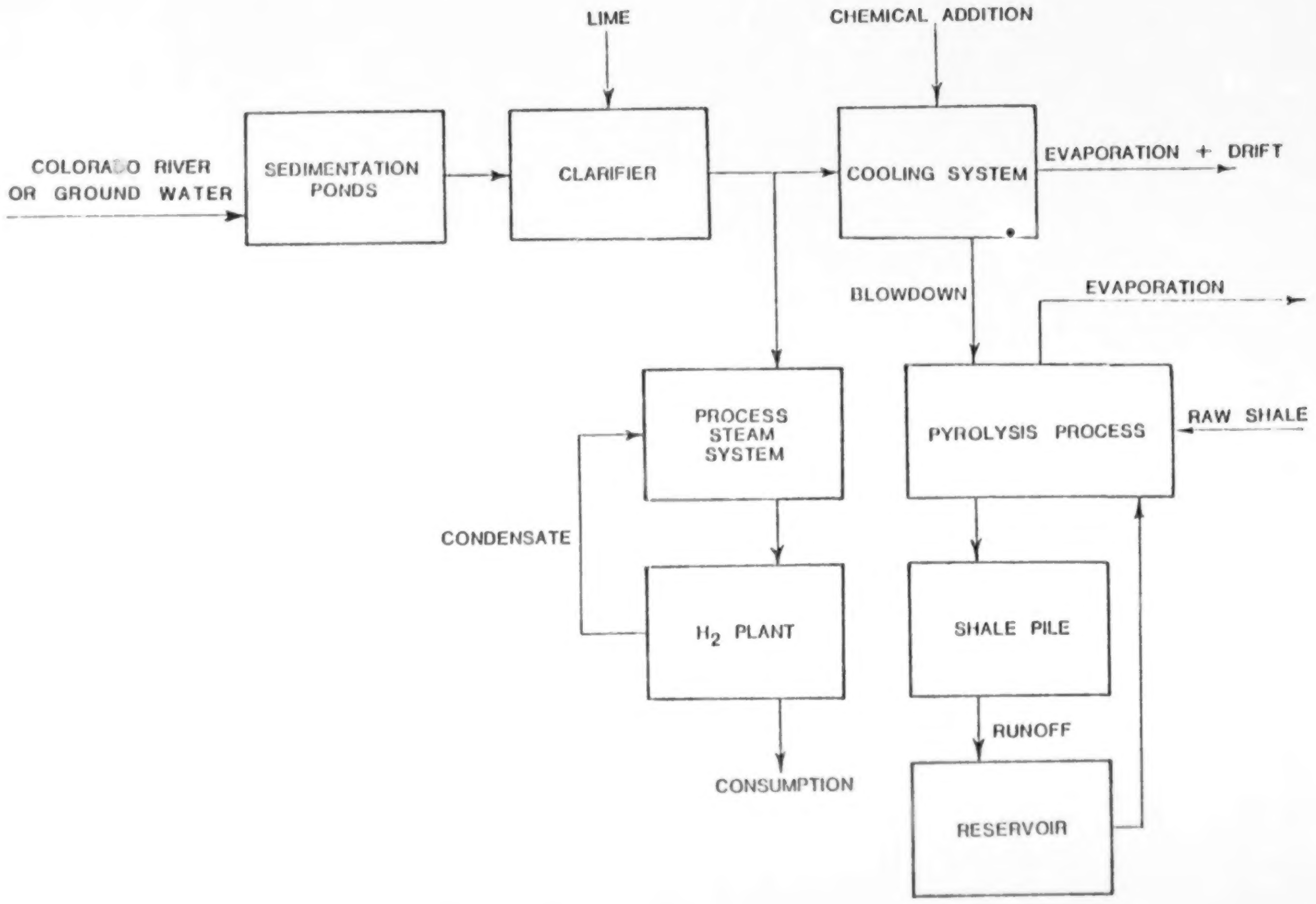


FIGURE 4.1-1 MAJOR WATER STREAMS FOR THE TOSCO II PROCESS

which can use poorer quality water. Processed shale disposal, which can accommodate the lowest quality water, is the final consumer of process waste waters.

Colony has presented the water systems for their TOSCO II plant (CO-175). As shown in previous sections, the heart of the oil shale plant is the pyrolysis and oil recovery unit. The water systems associated with the pyrolysis unit will be examined to identify areas with potential water problems.

4.1.1 Inlet Water

The quality of the water supply has a significant impact on the plant water systems. The plant must be designed to accommodate the inlet water characteristics to avoid equipment scaling and fouling.

The species given in Table 4.1-1 constitute the great majority of the ionic species in Colorado River water, which will be used in the Colony plant. Additional species (*e.g.*, iron, phosphate, boron, silicates, etc.) are also present, but exist in such comparatively small quantities that they have little effect on the system chemistry.

The raw river water entering the overall Colony water system will be treated with lime to reduce the concentration of calcium. Of this treated water, part will be used as a makeup stream to the cooling system, and the remainder will be used as process water.

Lime treatment of the river water will precipiate $CaCO_3$. For the Colony system's lime treatment step it was assumed that the calcium concentration could be reduced to 26 mg/ℓ in a lime treatment vessel of conventional capacity and retention time, giving a total Ca^{++}, Mg^{++} hardness of 42.5 mg/ℓ.

TABLE 4.1-1. COLORADO RIVER COMPOSITION*,**

Ca^{++}	70	mg/ℓ
MG^{++}	16.5	mg/ℓ
Na^{+}	110	mg/ℓ
HCO_3^-	158	mg/ℓ
$CO_3^=$	0	mg/ℓ
$SO_4^=$	135	mg/ℓ
Cl^-	150	mg/ℓ
NO_3^-	0.28	mg/ℓ
pH	8.0	
Temperature	2.25°C	

* Near DeBegue, Colorado

** August 1973 - September 1974 Average

4.1.2 Plant Water Stream Characterization

The major plant streams of interest are examined in this section.

Process Water

Because the Colony water system is designed to operate at zero discharge, all of the process water from retorting is eventually evaporated or consumed in moisturizing processed shale for disposal. Foul process water will be sent to a distillation cleaning process to remove NH_3 and H_2S before treating the processed shale. However, some residual NH_3 and H_2S will remain in the water after treatment.

Cooling Water

The Colony project's cooling system is composed of a multiple-cell induced-draft cooling tower and a network of piping over the entire processing area. A schematic of this system is given in Figure 4.1-2.

Fresh water must be continually supplied to the cooling system to make up for water lost during processing in the cooling tower. Evaporation occurring in the cooling tower concentrates the impurity species in the makeup water. Chemical additives may be introduced into the system to control the chemical characteristics of the cooling water. A purge from the cooling water recycle stream must also be maintained to remove impurity species at a rate sufficent to prevent scaling and fouling of the equipment.

Windage or drift from cooling towers carries dissolved impurity species from the recycle water loop along with the water droplets entrained in air. This reduces the required rate of liquid purge or blowdown, since it is a purge stream in itself. The drift rate is normally a function of the recycle water rate. The relationship between the cooling water concentration factor (CF), the evaporation rate (E), the drift rate (D), and the blowdown rate (B) is given below:

$$CF = \frac{E+B+D}{B+D} \qquad (4.1\text{-}1)$$

The concentration factor, or number of cycles of concentration, can also be expressed as the concentration of a given dissolved species in the cooling water recycle divided by the concentration of that species in the makeup water.

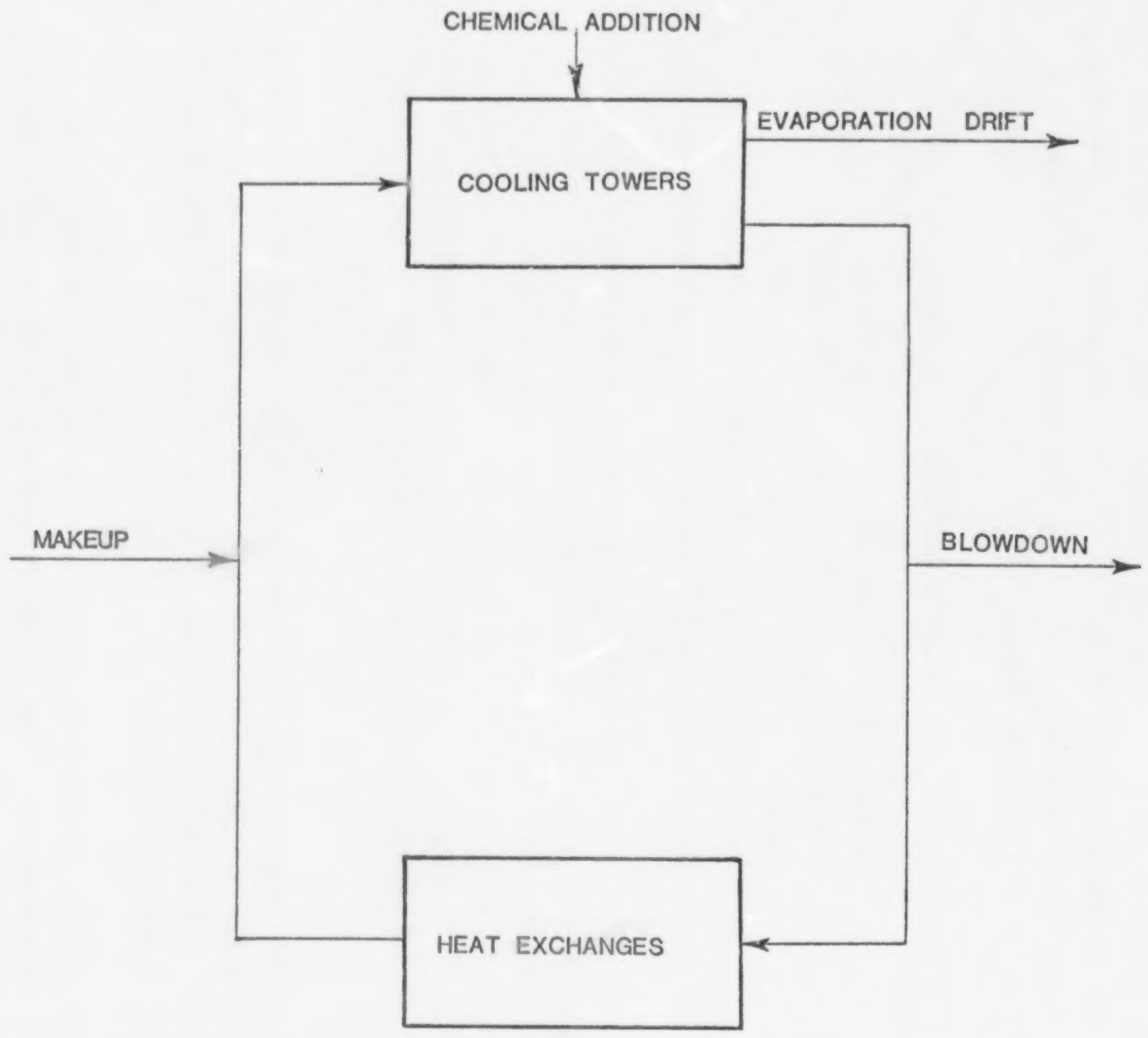


FIGURE 4.1-2 COOLING SYSTEM FOR THE TOSCO II PROCESS

Using the above formula and the proposed Colony cooling system flowrates (given in Table 4.1-2), the cooling system is found to operate at 4.7 cycles of concentration. This value is based on the assumption that the drift will be about 0.1 percent of the recirculating water, a typical approximation made for induced-draft wet cooling towers.

TABLE 4.1-2. OIL SHALE COOLING SYSTEM FLOWRATES

Evaporation and drift	1,530 gpm
Blowdown	370 gpm
Makeup	1,900 gpm
Recirculation Water	36,000 gpm

It is often desirable to reduce the blowdown stream from a cooling tower to minimize the waste water effluent from the cooling system. For a given evaporative cooling load, the blowdown rate is a function of the number of cycles of concentration of the cooling water. The relationship between blowdown rate and water concentration for the Colony cooling system is given in Figure 4.1-3.

A reduction in blowdown rate is generally achieved by increasing the cycles of concentration to the point at which calcium sulfate reaches saturation. Beyond this point, precipitation of calcium sulfate occurs.

It is common for acid (usually sulfuric acid) to be added to the recirculating water stream of a cooling cycle for pH control. The pH must be maintained low enough to prevent precipitation of calcium carbonate. Other chemicals are also usually added to the cooling water to inhibit biological degradation of the cooling towers and corrosion of the piping network.

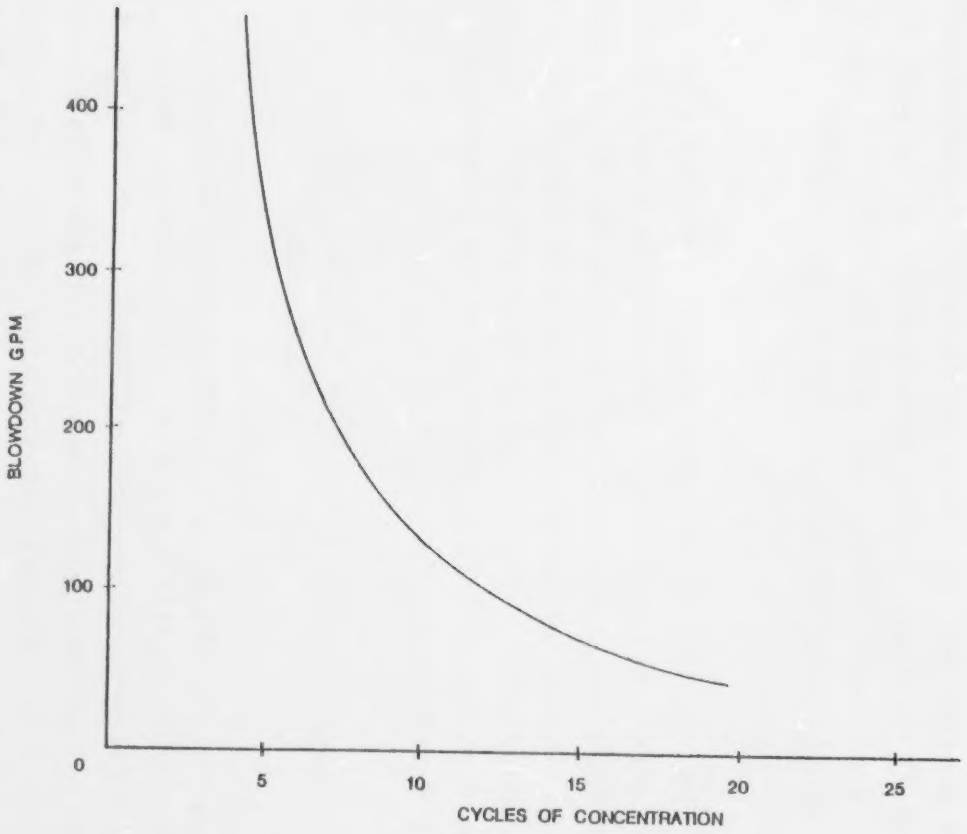


FIGURE 4.1-3 RELATIONSHIP BETWEEN BLOWDOWN RATE AND CYCLES OF CONCENTRATION

The Radian Equilibrium Program was used to model the effects of concentrating the recycled cooling water. This was accomplished by determining the equilibrium compositions of dissolved species in the cooling water at 5, 10, and 20 cycles of concentration. The concentrations of all species except $CO_3^=$ were increased by these concentration factors. The $CO_3^=$ ion is not affected by the concentration process in the same manner as the other ions because $CO_3^=$ is found to closely approach equilibrium with the CO_2 in the air during evaporation in the cooling tower. Therefore, a computer option was used that allowed the $CO_3^=$ ion to attain equilibrium in relation to the atmospheric partial pressure of CO_2.

The results of the equilibrium computer runs are listed in the Appendix. The most important results relate to the concentration of $CaSO_4 \cdot 2H_2O$ (calcium sulfate dihydrate), the chemical species most likely to scale under the Colony cooling system's operating conditions. The tendency toward forming scale is reflected in the value of $CaSO_4 \cdot 2H_2O$ relative saturation, which is defined by Equation 4.1-2.

$$RS_{CaSO_4 \cdot 2H_2O} = \frac{a_{Ca^{++}} \times a_{SO_4^=} \times (a_{H_2O})^2}{K_{CaSO_4 \cdot 2H_2O}} \qquad (4.1\text{-}2)$$

where $a_{Ca^{++}}$, $a_{SO_4^=}$, and a_{H_2O} are the chemical activities of the calcium ion, sulfate ion, and H_2O, respectively, and $K_{CaSO_4 \cdot 2H_2O}$ is the solubility product constant for calcium sulfate dihydrate. Precipitation can theoretically occur for any relative saturation greater than 1.0. However, in practice nucleation and scaling are found to require relative saturations of 1.2 to 1.4 in order to occur.

The tendency of Colony's cooling system to form calcium sulfate scale with increasing cycles of concentration is shown graphically in Figure 4.1-4. As the graph shows, the system's operating condition of 4.7 cycles of concentration corresponds to a $CaSO_4 \cdot 2H_2O$ relative saturation of about 0.15. Therefore, the cooling system is well removed from experiencing any problems with calcium sulfate scaling and, in fact, can afford to operate at higher cycles of concentration with higher relative saturations. This would permit a reduction in the flowrate of makeup water to the cooling system and a corresponding reduction in the blowdown rate. This analysis indicates that there will be a large margin of safety to maintain zero discharge if water system problems occur.

4.1.3 Potential Problems

Problems associated with the system may arise from species in the foul process water and the possibility of scaling during moisturization of processed shale.

Although foul water will be sent to a distillation to remove NH_3 and H_2S, some residual NH_3 and H_2S will remain in the water after treatment. This treated water will be used to moisturize the processed shale. Since large quantities of moisturized shale will be disposed of, there is the possibility of H_2S and NH_3 odor problems in the disposal area. Phenols, amines, and organic acids will also be in the process water used to moisturize shale. Some of these compounds may contribute to an odor problem.

During the mositurization of the shale, dissolution of inorganic species (such as CaO and MgO) may lead to scaling on the walls of the rotating drum moisturizer. The severity of this problem will depend on the composition of the shale, the composition of the process water, and the dissolution kinetics.

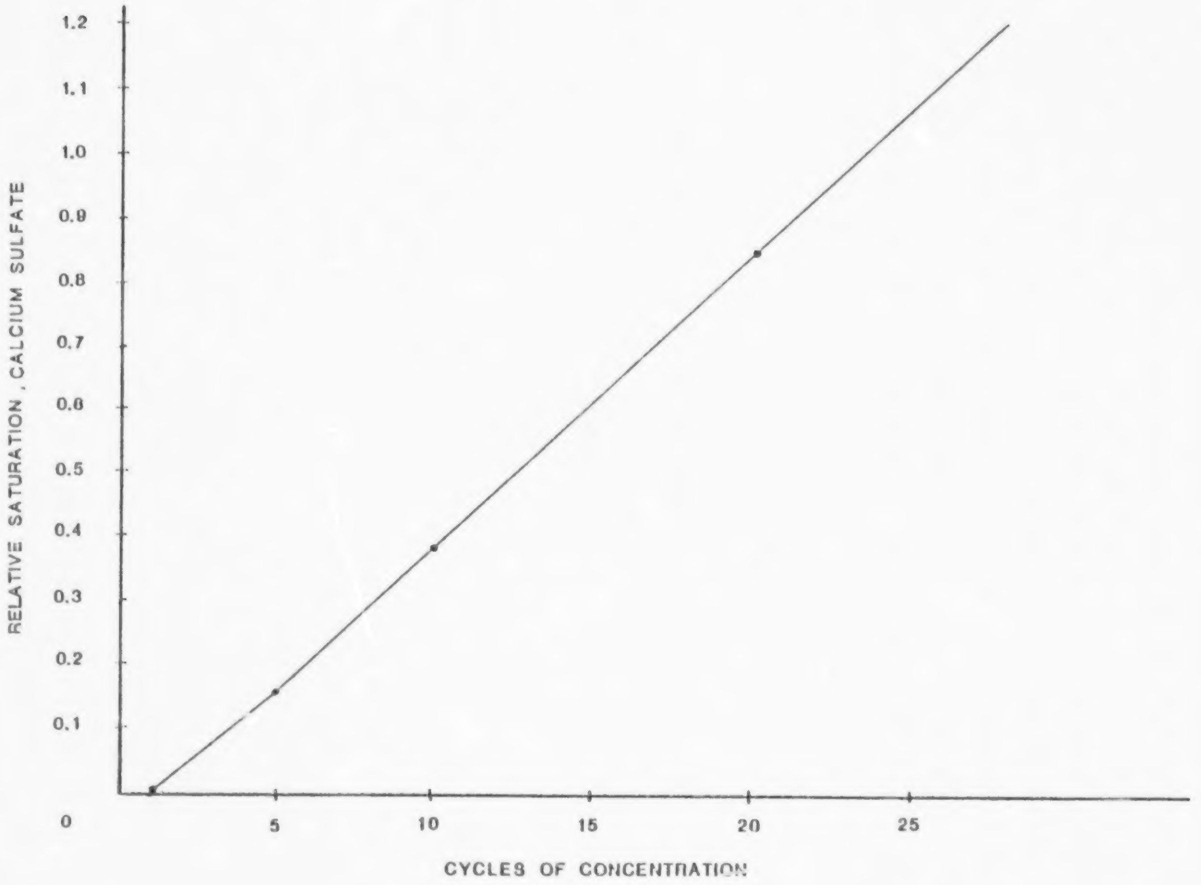


FIGURE 4.1-4 CALCIUM SULFATE SCALING PROFILE FOR THE COLONY COOLING TOWER

4.2 Lurgi Process Water System

The water system for a future Lurgi coal gasification plant is discussed in this section. The plant will be built as a joint venture of the Rochelle Coal Company and the Wyoming Coal Gas Company. The proposed plant site is the Powder River Basin of northeast Wyoming. Water supplies are relatively scarce in this area; and, as a result, water recycle is heavily stressed in the design of the plant facilities.

The plant's water stream network, shown in Figure 4.2-1, is relatively complex. In order to limit the use of raw water makeup to the plant, the water effluent streams from the gas cooling and gas cleaning processes are recycled for use as boiler feed water and cooling water. Both of these effluent streams are initially sent to a liquid-liquid extraction process, Lurgi's Phenosolvan process, to clean them of phenolic compounds. The gas cleaning liquor, designated the "minor" Phenosolvan effluent, is a stream rich in high-boiling organics, fatty acids, ammonia, coal dust and dissolved solids. The "major" Phenosolvan effluent is a wastewater stream from the gas cooling process and is rich in NH_3, H_2S, and low-boiling organics.

The proposed Wyoming plant will operate under one of two modes of recycle operation. The base case treats a majority of the major Phenosolvan effluent to cooling water quality for use as makeup to the cooling system. The rest of the major Phenosolvan effluent and all of the minor Phenosolvan effluent will be treated to boiler feedwater quality under this recycle mode. If boiler feedwater quality cannot be achieved, an alternate recycle mode will be to use all of the Phenosolvan effluent in the cooling system and redesign the cooling system to maintain zero discharge.

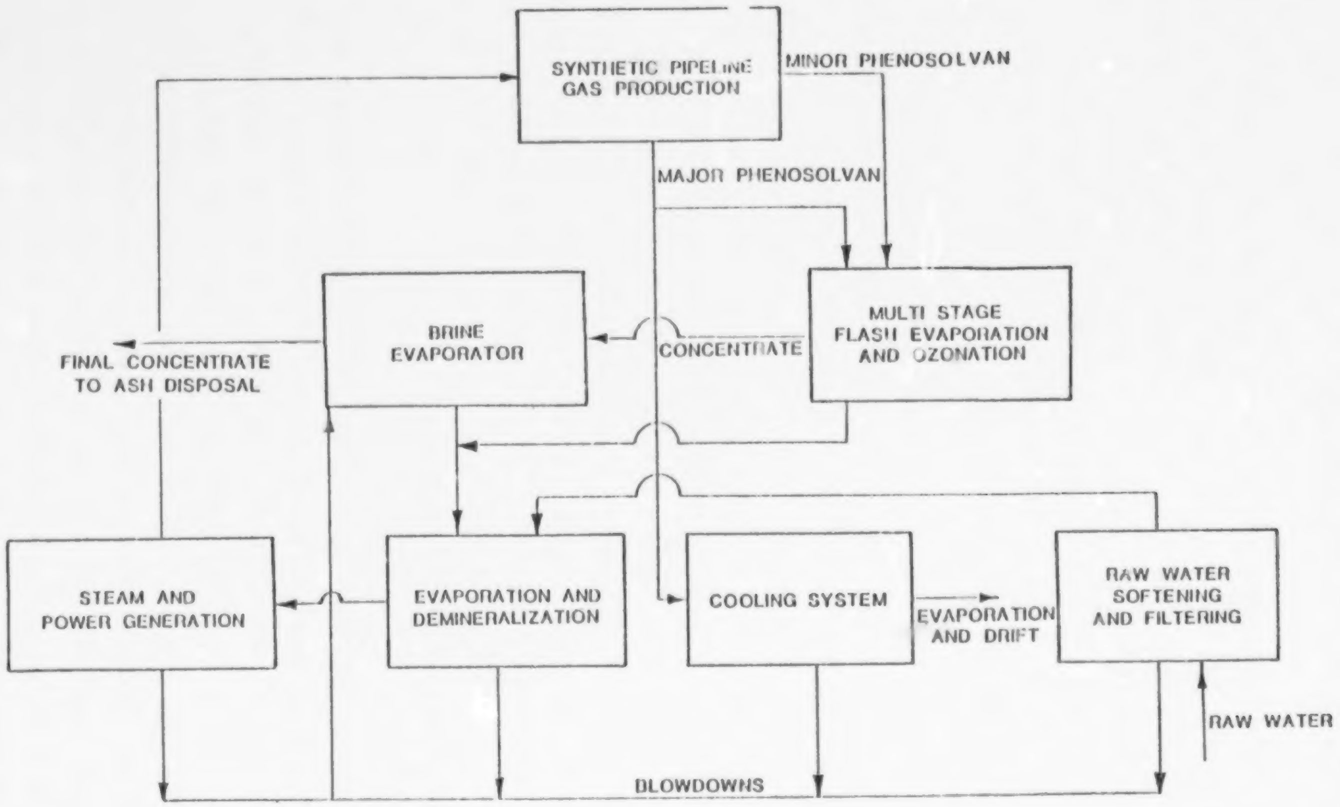

SYNTHETIC PIPELINE GAS PRODUCTION
MINOR PHENOSOLVAN
MAJOR PHENOSOLVAN
BRINE EVAPORATOR
CONCENTRATE
MULTI STAGE FLASH EVAPORATION AND OZONATION
FINAL CONCENTRATE TO ASH DISPOSAL
STEAM AND POWER GENERATION
EVAPORATION AND DEMINERALIZATION
COOLING SYSTEM
EVAPORATION AND DRIFT
RAW WATER SOFTENING AND FILTERING
RAW WATER
BLOWDOWNS

FIGURE 4.2-1 MAJOR WATER STREAMS FOR A LURGI COAL GASIFICATION PLANT

A basic feature of the water system which makes zero discharge operation feasible is the brine evaporation process. In this process the various blowdown or purge streams of high saline content can be treated to produce a distillate for use as boiler feedwater and a concentrated brine to be discharged to the ash sluicing system. The brine can be evaporated to almost any degree of concentration, making it possible to reclaim all of the process water, excepting that which is needed to moisturize the ash for disposal.

4.2.1 Inlet Water

A coal gasification plant can relay on two sources of water for makeup to its water system: river water and groundwater from nearby deep wells. The well water could be required if the gasification plant's water rights for diversion of river water will not guarantee a sufficient water supply during low-flow river conditions.

River water quality experiences some seasonal variation, with the winter quality being generally poorer. A typical winter analysis for the North Platte River is given in Table 4.2-1.

TABLE 4.2-1. NORTH PLATTE RIVER COMPOSITION - WINTER

Ca^{++}	61.9 mg/ℓ
Mg^{++}	21.5 mg/ℓ
Na^{+}	48.5 mg/ℓ
HCO_3^{-}	159.5 mg/ℓ
$SO_4^{=}$	193. mg/ℓ
Cl^{-}	14.4 mg/ℓ
Temperature	4.35°C

Groundwater is generally alkaline but is variable in quality. A representative composition for water coming from the deep wells is given in Table 4.2-2.

TABLE 4.2-2. DEEP WELL WATER COMPOSITION

Ca^{++}	179	mg/ℓ
Mg^{++}	35	mg/ℓ
Na^{+}	310	mg/ℓ
HCO_3^{-}	197	mg/ℓ
$SO_4^{=}$	1080.	mg/ℓ
Cl^{-}	6.8	mg/ℓ
pH	8.2	
Temperature	11°C	

Source: WY-007

The Wyoming plant's water system is designed to accommodate inlet water varying in quality from 600 to 1200 ppm total dissolved solids. Taking a weighted average of the river water composition and the groundwater composition, a composite inlet stream can be determined having a total dissolved solids value of 1200 ppm. When this composite stream is softened with lime and soda ash, the resultant stream entering the water system has a composition given in Table 4.2-3. This stream is then evaporated to produce high-quality boiler feedwater and a concentrate stream.

TABLE 4.2-3. TREATED MAKEUP TO WATER SYSTEM

Ca^{++}	35	mg/ℓ
Mg^{++}	15	mg/ℓ
Na^{+}	194	mg/ℓ
HCO_3^-	5.3	mg/ℓ
$SO_4^=$	686	mg/ℓ
Cl^-	10.18	mg/ℓ
Temperature	4.35°	
pH adjusted to 7.1		

4.2.2 Process Water Stream Characterization

The Wyoming plant's water system was not well-defined with respect to compositions and flowrates in its Environmental Impact Statement. The lack of specificity can be attributed to the unknown character of the major and minor Phenosolvan streams, especially the minor stream. The amount of dissolution of dust in this stream will be a function of the quality of the water entering the gas cleaning process, the type of coal, and the process operating conditions. In order to give an accurate description of the water system flowrates and compositions, samples will need to be taken of the actual process in operation. However, it is possible to make a reasonable approximation by using the following assumptions:

1) Based on Radian in-house data for aqueous dissolution of fly ash from coal, the minor (dusty liquor) Phenosolvan effluent stream will pick up around 3000 ppm of inorganic species. Much of it will be Ca^{++}.

2) The lime treatment process will discharge its underflow at about 10% solids.

3) Treated boiler feedwater will have about 0.5 ppm dissolved solids.

4) Purge from the boiler water treatment will be on the order of 5% of the inlet flow.

5) Cooling tower drift will be about 0.1% of recirculating flow.

6) Inlet water composition will be 1200 ppm total dissolved solids.

7) The brine concentrator concentrates to virtual dryness. (The water for ash sluicing mainly comes from raw water input).

8) Flash evaporation produces a water of about 10 ppm TDS.

Based on these assumptions, the estimated flows and compositions of the major water streams are given in Figure 4.2-2. The most questionable of these assumptions is necessarily the one pertaining to the composition of the minor Phenosolvan effluent. The nature of the particular species making up its total dissolved solids value will have a major effect on determining whether the minor Phenosolvan effluent can be treated to boiler feedwater quality.

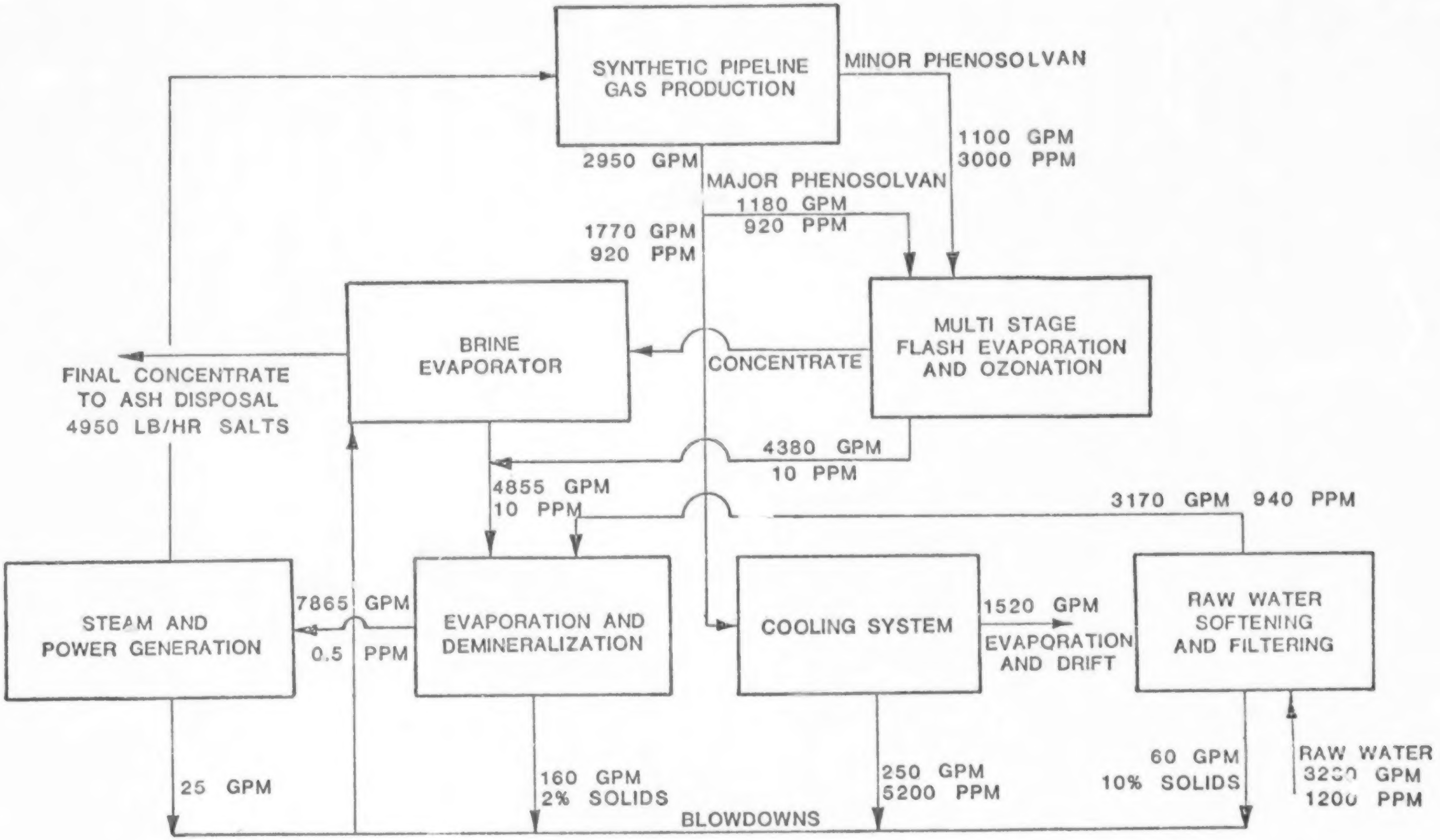


FIGURE 4.2-2 FLOW RATES FOR A LURGI WATER SYSTEM
(Concentration - ppm total dissolved solids inorganic species)

Based on the above assumptions, the cooling tower system operates at about 6 cycles of concentration. The tendency for calcium sulfate scaling in the Lurgi cooling towers is presented in Figure 4.2-3. This figure indicates that the cooling system is operating in a range that should be free from calcium sulfate scaling. However, the cycles can be increased only to about 9 before scaling would be a problem. This means that there is not a large margin of safety to maintain zero discharge if water system problems should occur. However, slipstream treatment to reduce excessive calcium concentrations in the recirculating cooling tower water may help alleviate unforeseen problems.

4.2.3 Potential Problems

The potential water system problem areas involve the Phenosolvan effluent streams, the system blowdown streams, and the ash sluicing line.

The minor Phenosolvan stream may be susceptible to $CaSO_4$ or $CaCO_3$ scaling, depending on the composition of the inlet water to the gas cleaning process and the amount of dissolution of the dust picked up during the cleaning process. Also, both Phenosolvan effluents have organic species in them which could cause problems with filming or foaming in the evaporators and the cooling towers. In addition, the Phenosolvan effluent streams will have residual phenolic compounds, NH_3, and H_2S; all of which can create toxicity and odor problems.

The blowdown or purge streams sent to the brine evaporator, some of which may be in slurry form, present the typical problem associated with piping concentrated streams: There is the possibility of scaling on the pipe walls due to dissolution

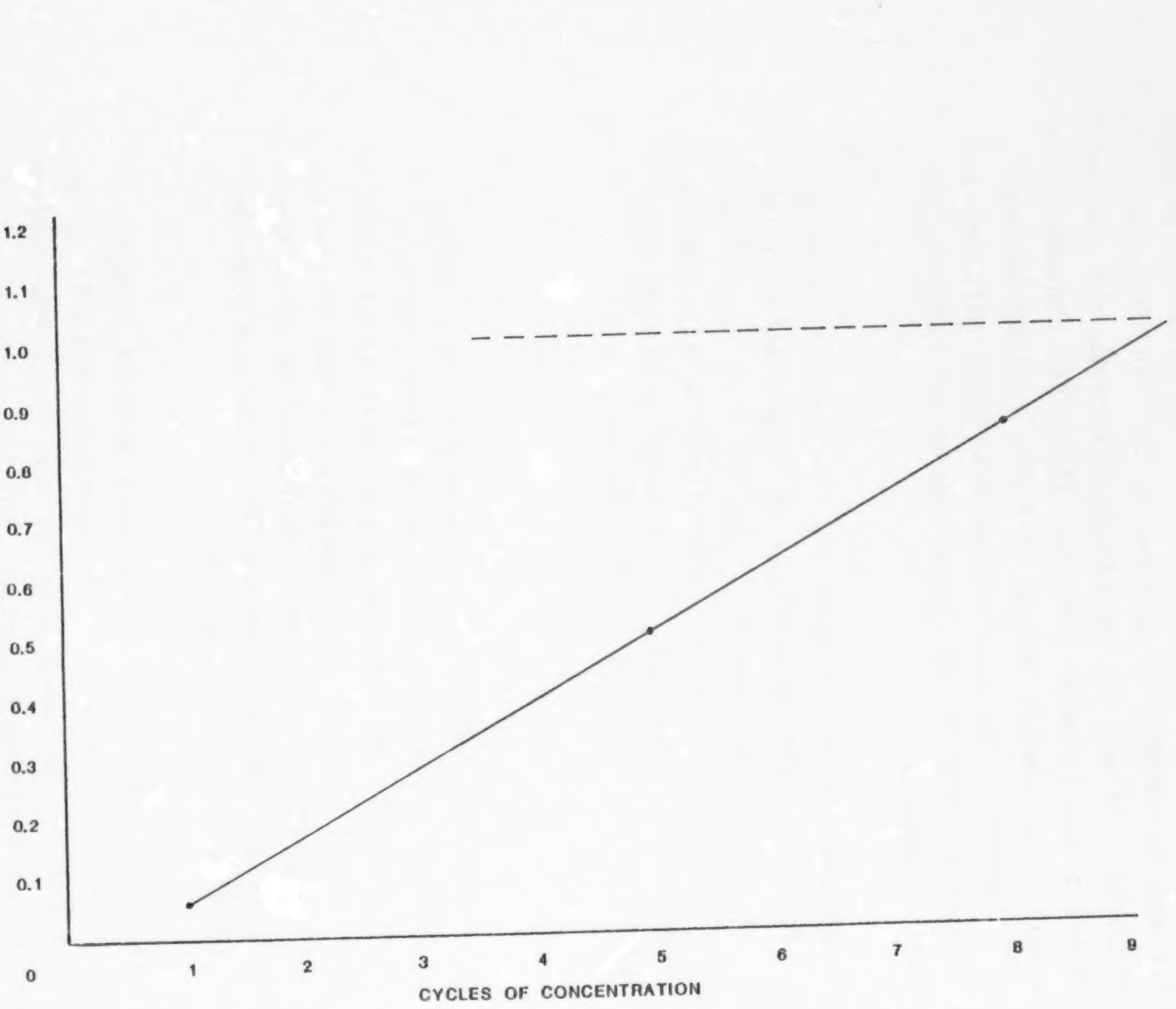


FIGURE 4.2-3 CALCIUM SULFATE SCALING PROFILE FOR THE LURGI COOLING TOWER

of solid species and subsequent reprecipitation. $CaSO_4$ scaling will be the major danger due to the high $SO_4^=$ concentration in the raw water inlet and the chance of picking up Ca^{++} in the minor Phenosolvan effluent. If all of the blowdown streams are collected in a common vessel prior to being fed into the brine concentration system, there will be a special danger of $CaSO_4$ scaling because of the high Ca^{++} concentration in the lime treatment effluent and the high $SO_4^=$ concentrations in the boiler feedwater blowdown and the cooling tower blowdown.

Problems that may occur with the ash sluicing also involve scaling. The ash might be expected to have a substantial amount of CaO. If the CaO is present in a form that can readily dissolve, there is a possibility of forming $CaCO_3$ scale, $Mg(OH)_2$ scale and/or $CaSO_4$ scale, depending on the composition of the sluice water, pH, and the kinetics of dissolution.

4.3 Summary

Based on the analysis of a representative oil shale project's water system, there appears to be no major problems confronting the application of their proposed water reuse strategies. They will mainly need to guard against scaling in their shale moisturization process. They will also need to clean their foul process water sufficiently to remove NH_3, H_2S, and phenols before using it to moisturize spent shale.

A Lurgi water system appears to have greater dangers of running into problems as a result of its relative complexity. Potential exists for scaling in the piping for the minor Phenosolvan stream (the gas cleaning effluent liquor), in the piping and vessels used to feed the various process blowdowns to the brine concentration system, and in the ash sluicing system. Whether or not these problems occur will depend on the specific nature of the coal used and the actual flow conditions, such as retention times for vessels and lines. In addition, odor problems may also arise from absorbed NH_3, H_2S, and phenols in the ash sluice liquor.

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1.0 INTRODUCTION

Descriptions of the computer models used in this study are presented in the Appendix. The computer models discussed are the Radian Equilibrium Program which considers the gas phase composition of chemical systems and the Radian Aqueous Inorganic Equilibrium Program which considers the aqueous chemistry of plant water systems.

The Radian Equilibrium Program was used to evaluate the trace element distributions in the synthetic fuels processes. The Radian Aqueous Inorganic Equilibrium Program was used to assess the water management strategies in the plant water systems for potential scaling problems. The computer printouts for the two equilibrium programs are also presented.

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2.0 RADIAN EQUILIBRIUM PROGRAM

The Radian Equilibrium Program is a computerized model that has the capability to predict the chemical equilibrium of systems composed of a single, ideal gas phase and several pure condensed phases. The basic computation yields the equilibrium composition and enthalpy for a given temperature and pressure. Optionally, the final temperature may be computed for adiabatic operation.

The technique used involves minimization of the total free energy of the system. The free energy of the system is written in terms of the standard-state free energies, the activity coefficients, if any, and the number of moles of each chemical species. The total free energy is then minimized according to the basic criterion for equilibrium.

The program is written in a generalized manner to allow for a flexible number of specified elements, condensed phases, and species. Up to ten elements, ten active condensed phases and four-hundred species can be considered.

TOSCO II Oil Shale Trace Element Analysis

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```
  SHALE OIL TRACE SPECIES

 TEMP =    755. DEG K           P =  1.0 ATM

 ELEMENT    GM-ATOMS INPUT  POTENTIAL(PI)     BALANCE ERROR
    C     =     6.7100       -1.10757              .775-06
    H     =    19.3200       -8.80039              .381-05
    O     =      .1700      -47.68515             -.279-07
    N     =      .0325      -14.78277             -.931-09
    CL    =      .0000      -42.19216              .000
    S     =      .3590      -13.92209              .820-07

 INITIAL ENTHALPY, H IN KCAL/KG  =                .00
 FINAL ENTHALPY, H IN KCAL/KG    =          -162.45
 CHANGE IN ENTHALPY, DELTA H     =          -162.45


 TOTAL MOLES OF GAS =   3.52677

 EQUILIBRIUM MOLE FRACTION GASES
 CH4            = .46717+00    CO          = .14264-02    N2          = .45682-02    HCL         = .28355-05
 H2S            = .10178+00    S2          = .29415-08    COS         = .12685-04    CS2         = .35628-07
 S8(G)          = .78320-30    CO2         = .95272-03    H2O         = .44858-01    H2          = .37915+00
 HCN            = .11716-08    NH3         = .78801-04    BENZENE     = .35238-15    (CH3)2S     = .62289-11
 CH3SH          = .76113-06    C2H4        = .19639-07    C2H6        = .65091-05    C3H8        = .29848-09
 C2H2           = .79230-13    C2N2        = .25124-21    C3O2        = .10708-20

 CONDENSED PHASES,MOLES/MOLE GAS
 C(GR)          =   1.43302

                TRACE ELEMENT DISTRIBUTION AMONG SPECIES, PERCENT


 BE  WT PPM IN FUEL =    35.000  GM-ATOM*1.E6 *********  PCT GAS =     .0   PI =  -50.54066
            BE(G)          =  .82-32    BE (S)         =  .00       BEO(G)         =  .00
            BEO(S)         =  .10+03    BE3O3 (G)      =  .00       BE4O4 (G)      =  .00
            BECL   (G)     =  .32-27    BEH2   (G)     =  .24-23    BECL2(G)       =  .30-14
            BECL2(L)       =  .00       BES(S)         =  .00       BEOH   (G)     =  .92-22
            BE(OH)2(G)     =  .14-06    BECO3(S)       =  .00       BE3N2(S)       =  .00
            BESO4          =  .00

 SE  WT PPM IN FUEL =      .080  GM-ATOM*1.E6 =    .8440  PCT GAS = 100.0   PI =  -20.51110
            SE     (G)     =  .39-06    SEH2           =  .10+03    SE2C           =  .17-07
            SECO           =  .65-21    SEO    (G)       =  .10-11    SEO2(G)        =  .18-19
            SE2    (G)     =  .50-05    SE(CH3)2         =  .28-06    SECS   (G)     =  .29-03
            SEC    (G)     =  .40-12

CD  WT PPM  IN FUEL =        .140  GM-ATOM*1.E6 =  1.0375  PCT GAS =   2.5     PI =  -21.84388
            CD(G)          =  .25+01    CDO(S)           =  .00       CDO (G)        =  .11-07
            CDS(S)         =  .97+02    CDCL(G)          =  .53-02    CDCL2(G)       =  .72-07
            CDCL2(S)       =  .00       CD(OH)2(G)       =  .36-08    CDH(G)         =  .67-24
            CD(CH3)2       =  .72-15    CDCO3            =  .00       CDSO4          =  .00

HG  WT PPM  IN FUEL =        .100  GM-ATOM*1.E6 =   .4153  PCT GAS = 100.0     PI =  -28.02285
            HG(G)          =  .10+03    HGO(G)           =  .14-13    HGS RED        =  .00
            HGCL   (G)     =  .16-12    HG(CL)2(L)       =  .00       HG(CL)2(G)     =  .42-13
            HGH    (G)     =  .26-11

AS  WT PPM  IN FUEL =      7.200  GM-ATOM*1.E6 = 80.0517  PCT GAS = 100.0     PI =   -7.54252
            AS(G)          =  .80-08    AS2(G)           =  .15-01    AS4(G)         =  .10+03
            ASO(G)         =  .32-09    ASCL3(G)         =  .53-15    ASH3           =  .41+00
            ASN(G)         =  .52-04

PB  WT PPM  IN FUEL =     10.000  GM-ATOM*1.E6 = 40.2046  PCT GAS = 100.0     PI =   -7.12410
            PB (G)         =  .66+00    (PB)2            =  .23-06    PBO(G)         =  .69-07
            PBO RED        =  .00       PBO2(S)          =  .00       PB3O4 (S)      =  .00
            PB(CL)         =  .54-01    PB(CL)2(S)       =  .00       PB(CL)2(G)     =  .99+02
            PB(CL)4        =  .12-25    PBH              =  .51-04    PB(CH3)4       =  .34-26
            PBCO3 (C)      =  .00       PBSO4            =  .00

B   WT PPM  IN FUEL =    140.000  GM-ATOM*1.E6 =*********  PCT GAS = 100.0     PI = -219.68232
            B  (G)         =  .00       H  (S)           =  .00       B2O3 (G)       =  .00
            BH3O3 (G)      =  .00       BHO2 (G)         =  .00       BO (G)         =  .00
            BO2 (G)        =  .00       BS (G)           =  .00       B2 (G)         =  .00
            B2CL4 (G)      =  .00       B2(OH)4 (S)      =  .00       B2(OH)4 (G)    =  .00
            B2H6 (G)       =  .00       B2O  (G)         =  .00       B2O2 (G)       =  .00
            B2O3 (L)       =  .00       BN (S)           =  .00       BN (G)         =  .00
            BH3 (G)        =  .00       BH2 (G)          =  .00       B(OH)2 (G)     =  .00
            BH (G)         =  .00       BCL3 (G)         =  .00       BCL2H (G)      =  .00
            BCL2 (G)       =  .00       BOCL (G)         =  .00       BCL (G)        =  .00
            BF (G)         =  .00       BOF (G)          =  .00       BF2 (G)        =  .00
            BHF2 (G)       =  .48-30    BOHF2 (G)        =  .42-25    BOF2  (G)      =  .00
            BF3  (G)       =  .10+03    B2F4 (G)         =  .00       B3F3O3 (G)     =  .00

CO  WT PPM  IN FUEL =     39.000  GM-ATOM*1.E6 =551.2512  PCT GAS =     .0     PI =  -10.00104
            COCL (G)       =  .17-16    COCL2(S)         =  .00       COCL2 (G)      =  .82-12
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                 COCL3 (G)     =  .41-23    CO2CL4 (G)    =  .13-25    COH (G)        =  .98-11
                 CO (G)        =  .74-18    CO (S)   B    =  .00       COO (S)        =  .00
                 COO (G)       =  .39-08    CO3O4 (S)     =  .00       COS (S)        =  .10+03
                 COCO3 (S)     =  .00       COSO4         =  .00

CR   WT PPM IN FUEL =   49.000  GM-ATOM*1.E6 =785.0027  PCT GAS =     .0   PI =  -25.77244
                 CR (G)        =  .25-23    CR (S)        =  .00       CRCL2 (G)      =  .69-17
                 CRN (G)       =  .00       CRO (G)       =  .50-26    CRO2 (G)       =  .92-27
                 CRO3 (G)      =  .00       CR2O3 (S)     =  .10+03    CRO3 (S)       =  .00
                 CRCL2 (S)     =  .00       CRCL3 (S)     =  .00       CR2(SO4)3      =  .00

CU   WT PPM IN FUEL =   15.000  GM-ATOM*1.E6 =196.6478  PCT GAS =     .0   PI =   -7.95340
                 CUCL2 (G)     =  .79-17    CUH (G)       =  .21-09    CUCL2 (S)      =  .00
                 CU  (S)       =  .00       CU  (G)       =  .25-11    CUO (S)        =  .00
                 CUO (G)       =  .65-22    CU2           =  .21-20    CU2O (S)       =  .00
                 CUCL (L)      =  .00       CUCL (G)      =  .15-08    CUS  (S)       =  .00
                 CU2S (S)      =  .10+03    CUCO3  (S)    =  .00       CUSO4          =  .00

GE   WT PPM IN FUEL =     .400  GM-ATOM*1.E6 =  4.5906  PCT GAS =  87.5   PI =  -14.65172
                 GE  (G)       =  .55-15    GE  (S)       =  .00       GEH (G)        =  .5?-07
                 GEO (G)       =  .23+00    GEO2 (S)      =  .00       GES  (S)       =  .00
                 GES2 (S)      =  .13+02    GES  (G)      =  .87+02    GEH4 (G)       =  .12-07
                 GECL (G)      =  .90-14    GECL4 (G)     =  .25-17    GE(SO4)2       =  .00

MN   WT PPM IN FUEL =   34.000  GM-ATOM*1.E6 =515.5265  PCT GAS =     .0   PI =  -39.42186
                 MN  (G)       =  .42-17    MNO  (S)      =  .00       MNO (G)        =  .15-23
                 MNCL2 (G)     =  .53-10    MNH (G)       =  .38-18    MN2O3 (S)      =  .00
                 MN3O4 (S)     =  .00       MNS  (S)      =  .10+03    MNS2  (S)      =  .00
                 MNCL  (G)     =  .16-14    MNCL2 (S)     =  .00       MNSO4          =  .00
                 MN2(SO4)3     =  .00

MO   WT PPM IN FUEL =    4.900  GM-ATOM*1.E6 = 42.5443  PCT GAS =     .0   PI =  -11.24601
                 MOCL2 (G)     =  .35-05    MOCL  (G)     =  .24-16    MO (S)         =  .00
                 MO (G)        =  .00       MOO (G)       =  .00       MOO2 (S)       =  .00
                 MOO2 (G)      =  .40-23    MOO3 (S)      =  .00       MOO3 (G)       =  .25-19
                 MOO2CL2 (G)   =  .67-13    MOCL4 (G)     =  .34-23    MOS2 (S)       =  .10+03
                 MO(SO4)3      =  .00

NI   WT PPM IN FUEL =    1.000  GM-ATOM*1.E6 =156.9722  PCT GAS =     .0   PI =   -4.73386
                 NI (S)B       =  .10+03    NI (G) A      =  .31-15    NIO (G)        =  .16-25
                 NIO (S) A     =  .00       NICO3 (S)     =  .00       NI(CO)4 (G)    =  .90-15
                 NICL2 (S)     =  .00       NICL (G)      =  .19-12    NICL2 (G)      =  .77-12
                 NISO4         =  .00
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SB  WT PPM IN FUEL =      .390  GM-ATOM*1.E6 =  2.6683  PCT GAS = 100.0   PI =   -7.91231
           SB (S)        =  .00        SB (G)         =  .20-03   SB2 (G)        =  .16+00
           SB4 (G)       =  .38+01     SBO (G)        =  .13-16   SB2O3 (S)      =  .00
           SB2O4 (S)     =  .00        SB2S3 (S)      =  .00      SBH3  (G)      =  .11-03
           SBCL (G)      =  .98+02     SBCL2 (G)      =  .55-10   SBCL3 (G)      =  .26-09
           SB2(SO4)3     =  .00

SN  WT PPM IN FUEL =      .110  GM-ATOM*1.E6 =   .7720  PCT GAS =  55.0   PI =  -13.54060
           SN  (G)       =  .13-08     SNO  (S)       =  .00      SNO (G)        =  .82-05
           SNO2 (S)      =  .00        SNS  (S) A     =  .45+02   SNS2  (S)      =  .00
           SNS  (G)      =  .55+02     SNCL2 (G)      =  .13-03   SNCL4 (G)      =  .74-17
           SNH  (G)      =  .12-03     SNCL  (G)      =  .25-09   SN(SO4)2       =  .00

U   WT PPM IN FUEL =      .990  GM-ATOM*1.E6 =  3.4646  PCT GAS =     .0   PI =  -89.24722
           UCL3  (S)     =  .00        UH3    (S)     =  .00      U  (S)    A    =  .20
           U(CO3)2 (S)   =  .00        U(SO4)2 (S)    =  .00      UCL5  (L)      =  .00
           UCL4  (S)     =  .02        UOCL2  (S)     =  .00      UOCL3  (S)     =  .00
           UOCL (S)      =  .00        UCL6 (G)       =  .00      US    (S)      =  .00
           UO3  (S)      =  .00        U4O9 (S)       =  .00      U3O8 (S)       =  .00
           UO2  (S)      =  .10+03     UO2CL2 (S)     =  .00      UO2 (G)        =  .16-27

ZN  WT PPM IN FUEL =   13.000  GM-ATOM*1.E6 =165.6570  PCT GAS =     .0   PI =  -27.27693
           ZN  (G)       =  .16-05     ZNCL (G)       =  .11-13   ZNCL2 (G)      =  .66-09
           ZNCL2 (L)     =  .00        ZNH (G)        =  .22-16   ZNO  (G)       =  .56-13
           ZNO  (S)      =  .00        ZNS  (S)       =  .10+03   ZNCO3 (S)      =  .00
           ZNSO4         =  .00

BA  WT PPM IN FUEL =   32.000  GM-ATOM*1.E6 =194.0577  PCT GAS =     .0   PI = -237.30423
           BAS  (G)      =  .00        BAS  (S)       =  .00      BACL2 (S)      =  .00
           BACL2 (G)     =  .00        BAO   (S)      =  .00      BAO   (G)      =  .00
           BAH  (G)      =  .00        BACO3 (S)A     =  .00      BA  (S)  B     =  .00
           BA  (G)       =  .00        BACL(G)        =  .00      BASO4 (S)      =  .00
           BAF (G)       =  .00        BAF2 (S) A     =  .10+03   BAF2 (G)       =  .32-11
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3.0 RADIAN AQUEOUS INORGANIC EQUILIBRIUM PROGRAM

The Radian Aqueous Inorganic Equilibrium Program is a computerized model that provides the capability to predict aqueous process chemistry. The program provides this capability based upon the specification of nine key species commonly present in plant water systems. These key species are: CaO, MgO, Na_2O, SO_2, SO_3, CO_2, N_2O_5, HCl, and H_2O.

Numerous chemical equilibria for the system are analysed. There are 44 dissociation-type equations, 11 solubility product relations, and 8 gas solubility equations. Equilibrium relationships are expressed as activities using products of individual molalities and activity coefficients. The activity coefficients are correlated with ionic strengths to account for solution non-ideality. Deviations from ideality can be quite significant in water systems, especially when water is recycled and reused.

The program can be applied to water management systems to predict the scaling potential for such species as calcium sulfate dihydrate, calcium carbonate and magnesium hydroxide. Radian laboratory experiments and pilot plant tests indicate that the scaling potential of a chemical species can be correlated with the relative saturation of that species in a solution. The aqueous inorganic equilibrium program will predict these relationships.

Water Analyses for the TOSCO II and Lurgi Systems

Colony Water System - 5 cycles of concentration

```
18 JUN 76    18:26:48,779                                   TEMPERATURE     2,240 DEG. C,
                                    INPUT SPECIES (MOLES)

                     H2O  = 5,55062+01            HCl  = 2,32003-02
                     CAO  = 3,26000-03            CO2  = 0,00000
                     MGO  = 3,39350-03            N2O3 = 0,00000
                     NA2O = 1,20000-02            N2O5 = 0,00000
                                                  SO2  = 0,00000
                                                  SO3  = 7,02500-03

               PCO2 = 3,33000-04  ATM,
                              AQUEOUS SOLUTION EQUILIBRIA

               COMPONENT          MOLALITY           ACTIVITY    ACTIVITY COEFFICIENT

                H+                1,598-07           1,374-07          8,599-01
                H2O                                                    9,990-01
                H2CO3             2,139-05           2,156-05          1,008+00
                HCO3-             5,337-05           4,434-05          8,307-01
                HSO4-             2,096-08           1,741-08          8,304-01

                CA++              2,705-03           1,315-03          4,862-01
                CAOH+             3,271-10           2,716-10          8,304-01
                CAHCO3+           1,053-06           8,744-07          8,304-01
                CACO3             1,261-08           1,271-08          1,008+00
                CASO4             5,532-04           5,577-04          1,008+00

                MG++              2,855-03           1,441-03          5,048-01
                MGOH+             4,979-09           4,134-09          8,304-01
                MGHCO3+           6,020-07           4,999-07          8,304-01
                MGCO3             2,135-08           2,152-08          1,008+00
                MGSO4             5,371-04           5,415-04          1,008+00

                NA+               2,372-02           1,990-02          8,391-01
                NAOH              5,516-11           5,561-11          1,008+00
                NAHCO3            8,623-07           8,693-07          1,008+00
                NACO3-            1,303-08           1,082-08          8,304-01
                NASO4-            2,730-04           2,267-04          8,304-01

                OH-               1,250-08           1,038-08          8,304-01
                CL-               2,320-02           1,917-02          8,265-01
                CO3--             1,732-08           8,245-09          4,761-01




                SO4--             5,660-03           2,527-03          4,465-01

               COMPONENT          MOLALITY       ACTIVITY PRODUCT  RELATIVE SATURATION

                CA(OH)2(S)        0,000              1,417-19          1,673-14
                CACO3(S)          0,000              1,004-11          7,720-04
                CASO4(S)          0,000              3,318-06          1,619-01
                MG(OH)2(S)        0,000              1,553-19          9,103-09
                MGCO3(S)          0,000              1,182-11          2,989-07

                CO2  = 7,73589-05  MOLES

                             MOLECULAR WATER = 1,00021+00 KGS,

            PH =  6,8621          IONIC STRENGTH = 4,60632-02        RES, E,N, =  -2,701-08
```

Colony Water System - 10 cycles of concentration

```
18 JUN 76    18:26:49,996                                      TEMPERATURE     2,240 DEG, C,
                                    INPUT SPECIES (MOLES)

                        H2O  = 5,55062+01              HCL  = 4,64000-02
                        CAO  = 6,52000-03              CO2  = 0,00000
                        MGO  = 6,78700-03              N2O3 = 0,00000
                        NA2O = 2,40000-02              N2O5 = 0,00000
                                                       SO2  = 0,00000
                                                       SO3  = 1,42500-02

             PCO2 = 3,32046-04  ATM,
                              AQUEOUS SOLUTION EQUILIBRIA

            COMPONENT          MOLALITY          ACTIVITY     ACTIVITY COEFFICIENT

             H+                8,908-08          7,485-08            8,403-01
             H2O                                                     9,981-01
             H2CO3             2,121-05          2,154-05            1,016+00
             HCO3-             1,030-04          8,130-05            7,892-01
             HSO4-             1,760-08          1,394-08            7,922-01

             CA++              5,222-03          2,109-03            4,040-01
             CAOH+             1,008-09          7,986-10            7,922-01
             CAHCO3+           3,245-06          2,571-06            7,922-01
             CACO3             6,751-08          6,858-08            1,016+00
             CASO4             1,294-03          1,315-03            1,016+00

             MG++              5,499-03          2,360-03            4,291-01
             MGOH+             1,567-08          1,241-08            7,922-01
             MGHCO3+           1,894-06          1,501-06            7,922-01
             MGCO3             1,168-07          1,166-07            1,016+00
             MGSO4             1,283-03          1,303-03            1,016+00

             NA+               4,717-02          3,790-02            8,035-01
             NAOH              1,912-10          1,942-10            1,016+00
             NAHCO3            2,988-06          3,036-06            1,016+00
             NACO3-            8,751-08          6,933-08            7,922-01
             NASO4-            8,014-04          6,349-04            7,922-01

             OH-               2,403-08          1,904-08            7,922-01
             CL-               4,638-02          3,630-02            7,826-01
             CO3--             7,154-08          2,775-08            3,879-01




             SO4--             1,067-02          3,716-03            3,484-01

            COMPONENT          MOLALITY       ACTIVITY PRODUCT  RELATIVE SATURATION

             CA(OH)2(S)        0,000             7,642-19            9,021-14
             CACO3(S)          0,000             5,852-11            4,166-03
             CASO4(S)          0,000             7,807-05            3,811-01
             MG(OH)2(S)        0,000             8,550-19            5,011-08
             MGCO3(S)          0,000             6,465-11            1,639-06

             CO2  = 1,32747-04  MOLES

                           MOLECULAR WATER = 1,00042+00 KGS,

        PH =  7,1258        IONIC STRENGTH = 9,00006-02        RES, E,N, =  -6,426-08
```

Colony Water System - 20 cycles of concentration

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18 JUN 76    18:26:44,786                                    TEMPERATURE     2,240 DEG, C,
                                   INPUT SPECIES (MOLES)

                   H2O  = 5,55062+01               HCL  = 9,28000-02
                   CAO  = 1,30400-02               CO2  = 0,00000
                   MGO  = 1,35740-02               N2O3 = 0,00000
                   NA2O = 4,80000-02               N2O5 = 0,00000
                                                   SO2  = 0,00000
                                                   SO3  = 2,81000-02

          PCO2 = 3,30000-04  ATM,
                             AQUEOUS SOLUTION EQUILIBRIA

         COMPONENT          MOLALITY             ACTIVITY    ACTIVITY COEFFICIENT

          H+                5,039-08             4,200-08           8,336-01
          H2O                                                       9,962-01
          H2CO3             2,085-05             2,150-05           1,031+00
          HCO3-             1,943-04             1,446-04           7,443-01
          HSO4-             1,444-08             1,093-08           7,571-01

          CA++              1,017-02             3,379-03           3,324-01
          CAOH+             3,006-09             2,276-09           7,571-01
          CAHCO3+           9,676-06             7,326-06           7,571-01
          CACO3             3,377-07             3,483-07           1,031+00
          CASO4             2,854-03             2,943-03           1,031+00

          MG++              1,065-02             3,882-03           3,645-01
          MGOH+             4,797-08             3,632-08           7,571-01
          MGHCO3+           5,800-06             4,391-06           7,571-01
          MGCO3             5,997-07             6,185-07           1,031+00
          MGSO4             2,905-03             2,996-03           1,031+00

          NA+               9,368-02             7,199-02           7,685-01
          NAOH              6,361-10             6,561-10           1,031+00
          NAHCO3            9,943-05             1,025-05           1,031+00
          NACO3-            5,512-07             4,173-07           7,571-01
          NASO4-            2,225-03             1,685-03           7,571-01

          OH-               4,472-08             3,386-08           7,571-01
          CL-               9,272-02             6,812-02           7,346-01
          CO3--             2,[illegible]56-07             8,795-08           3,068-01




           SO4--            2,009-02             5,193-03           2,584-01

          COMPONENT         MOLALITY        ACTIVITY PRODUCT  RELATIVE SATURATION

           CA(OH)2(S)       0,000                3,874-18          4,573-13
           CACO3(S)         0,000                2,972-10          2,116-02
           CASO4(S)         0,000                1,741-05          8,500-01
           MG(OH)2(S)       0,000                4,451-18          2,609-07
           MGCO3(S)         0,000                3,350-10          8,470-06

           CO2  = 2,42518-04  MOLES

                          MOLECULAR WATER = 1,00083+00 KGS,

   PH =  7,3767          IONIC STRENGTH = 1,76237-01        RES, E,N, =  -7,078-08
```

Lurgi System - raw water

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21 JUN 76    11:30:22,939                                     TEMPERATURE     4,340 DEG. C.
                                     INPUT SPECIES (MOLES)

                   H2O  = 5,55062+01               HCL  = 2,87000-04
                   CAO  = 8,73300-04               CO2  = 0,00000
                   MGO  = 6,17000-04               N2O3 = 0,00000
                   NA2O = 5,84000-03               N2O5 = 0,00000
                                                   SO2  = 0,00000
                                                   SO3  = 7,14200-03

            PCO2 = 3,30000-04  ATM.
                        AQUEOUS SOLUTION EQUILIBRIA

           COMPONENT         MOLALITY            ACTIVITY     ACTIVITY COEFFICIENT

             H+              8,940-08            7,931-08            8,871-01
             H2O                                                     9,997-01
             H2CO3           2,016-05            2,023-05            1,004+00
             HCO3-           8,749-05            7,628-05            8,718-01
             HSO4-           1,773-08            1,544-08            8,707-01

             CA++            6,408-04            3,739-04            5,834-01
             CAOH+           1,911-10            1,664-10            8,707-01
             CAHCO3+         5,006-07            4,359-07            8,707-01
             CACO3           1,184-08            1,188-08            1,004+00
             CASO4           2,320-04            2,329-04            1,004+00

             MG++            4,642-04            2,765-04            5,956-01
             MGOH+           1,994-09            1,736-09            8,707-01
             MGHCO3+         1,923-07            1,675-07            8,707-01
             MGCO3           1,355-08            1,361-08            1,004+00
             MGSO4           1,526-04            1,531-04            1,004+00

             NA+             1,148-02            1,006-02            8,763-01
             NAOH            5,934-11            5,956-11            1,004+00
             NAHCO3          7,535-07            7,563-07            1,004+00
             NACO3-          2,044-08            1,780-08            8,707-01
             NASO4-          1,938-04            1,688-04            8,707-01

             OH-             2,525-08            2,199-08            8,707-01
             CL-             2,870-04            2,495-04            8,695-01
             CO3--           4,555-08            2,632-08            5,778-01




              SO4--             6,564-03            3,665-03            5,583-01

             COMPONENT          MOLALITY         ACTIVITY PRODUCT  RELATIVE SATURATION

              CA(OH)2(S)        0,000               1,807-19            2,208-14
              CACO3(S)          0,000               9,[illegible]-12            7,780-04
              CASO4(S)          0,000               1,369-06            6,511-02
              MG(OH)2(S)        0,000               1,337-19            8,077-09
              MGCO3(S)          0,000               7,265-12            1,951-07

              CO2  = 1,29186-04  MOLES

                              MOLECULAR WATER = 1,00000+00 KGS.

        PH =  7,1007          IONIC STRENGTH = 2,13643-02         RES. E.N. =   4,657-09
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Lurgi System - 5 cycles of concentration

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21 JUN 76     11:39:26,150
                                                           TEMPERATURE     4,340 DEG. C.
                                 INPUT SPECIES (MOLES)

                 H2O  = 5,55062+01                 HCL  = 1,43500-03
                 CAO  = 4,36650-03                 CO2  = 0,00000
                 MGO  = 3,08500-03                 N2O3 = 0,00000
                 NA2O = 2,90000-02                 N2O5 = 0,00000
                                                   SO2  = 0,00000
                                                   SO3  = 3,57100-02

          PCO2 = 3,30004-04  ATH.
                          AQUEOUS SOLUTION EQUILIBRIA

          COMPONENT         MOLALITY          ACTIVITY     ACTIVITY COEFFICIENT

           H+               2,137-07          1,791-07          8,378-01
           H2O                                                  9,985-01
           H2CO3            1,986-05          2,021-05          1,018+00
           HCO3-            4,313-05          3,374-05          7,823-01
           HSO4-            1,219-07          9,587-08          7,863-01

           CA++             2,631-03          1,031-03          3,919-01
           CAOH+            2,581-10          2,029-10          7,863-01
           CAHCO3+          6,762-07          5,317-07          7,863-01
           CACO3            6,309-09          6,419-09          1,018+00
           CASO4            1,735-03          1,766-03          1,018+00

           MG++             1,898-03          7,931-04          4,179-01
           MGOH+            2,801-09          2,203-09          7,863-01
           MGHCO3+          2,703-07          2,125-07          7,863-01
           MGCO3            7,516-09          7,648-09          1,018+00
           MGSO4            1,187-03          1,208-03          1,018+00

           NA+              5,540-02          4,423-02          7,978-01
           NAOH             1,137-10          1,157-10          1,018+00
           NAHCO3           1,444-06          1,469-06          1,018+00
           NACO3-           1,948-08          1,531-08          7,863-01
           NASO4-           2,592-03          2,038-03          7,863-01

           OH-              1,237-08          9,726-09          7,863-01
           CL-              1,435-03          1,113-03          7,754-01
           CO3--            1,377-08          5,156-09          3,746-01



           SO4--            3,019-02          1,008-02          3,337-01

          COMPONENT         MOLALITY      ACTIVITY PRODUCT  RELATIVE SATURATION

           CA(OH)2(S)       0,000             9,752-20          1,191-14
           CACO3(S)         0,000             5,315-12          4,203-04
           CASO4(S)         0,000             1,036-05          4,925-01
           MG(OH)2(S)       0,000             7,502-20          4,533-09
           MGCO3(S)         0,000             4,059-12          1,090-07

          CO2  = 6,54303-05  MOLES

                       MOLECULAR WATER = 1,00001+00 KGS.

    PH =  6,7470        IONIC STRENGTH = 9,91832-02        RES. E.N. =  -2,515-08
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Lurgi System - 8 cycles of concentration

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22 JUN 76     11:17:24.635                                TEMPERATURE      4,340 DEG. C.
                                   INPUT SPECIES (MOLES)

                  H2O   = 5.55062+01           HCL   = 3.00000-03
                  CAO   = 6.98640-03           CO2   = 0.00000
                  MGO   = 4.93670-03           N2O3  = 0.00000
                  NA2O  = 4.67750-02           N2O5  = 0.00000
                                               SO2   = 0.00000
                                               SO3   = 5.71360-02

      PCO2 = 3.30016-04  ATM.
                    AQUEOUS SOLUTION EQUILIBRIA

     COMPONENT            MOLALITY              ACTIVITY     ACTIVITY COEFFICIENT

      H+                  8,689-08              7,236-08          8,328-01
      H2O                                                         9,976-01
      H2CO3               1,965-05              2,019-05          1,028+00
      HCO3-               1.110-04              8,344-05          7,520-01
      HSO4-               6,454-08              4,920-08          7,623-01

      CA++                4,045-03              1,389-03          3,433-01
      CAOH+               8.857-10              6,759-10          7.623-01
      CAHCO3+             2,323-06              1,771-06          7.623-01
      CACO3               5,149-08              5,292-08          1.028+00
      CASO4               2,939-03              3,021-03          1,028+00

      MG++                2,896-03              1,083-03          3,741-01
      MGOH+               9,759-09              7,440-09          7,623-01
      MGHCO3+             9,416-07              7.178-07          7,623-01
      MGCO3               6,221-08              6,393-08          1.028+00
      MGSO4               2,039-03              2,096-03          1.028+00

      NA+                 8,029-02              6,834-02          7,741-01
      NAOH                4,305-10              4,424-10          1.028+00
      NAHCO3              5.467-06              5.618-05          1.028+00
      NACO3-              1,901-07              1.449-07          7.623-01
      NASO4-              5,251-03              4,003-03          7,623-01

      OH-                 3,155-08              2,405-08          7,623-01
      CL-                 3,000-03              2,229-03          7.429-01
      CO3--               9,867-08              3,155-08          3,198-01




     SO4--                4,691-02            1,280-02           2,728-01

     COMPONENT            MOLALITY       ACTIVITY PRODUCT  RELATIVE SATURATION

      CA(OH)2(S)          0,000                8,032-19           9,812-14
      CACO3(S)            0,000                4,381-11           3,464-03
      CASO4(S)            0,000                1,769-05           8,411-01
      MG(OH)2(S)          0,000                6,266-19           3,786-08
      MGCO3(S)            0,000                3,378-11           9,073-07

      CO2   = 1,39743-04  MOLES

                    MOLECULAR WATER = 1,00043+00 KGS,

PH =  7,1405        ·IONIC STRENGTH = 1,56020-01       RES. E.N. =  -1,406-07
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